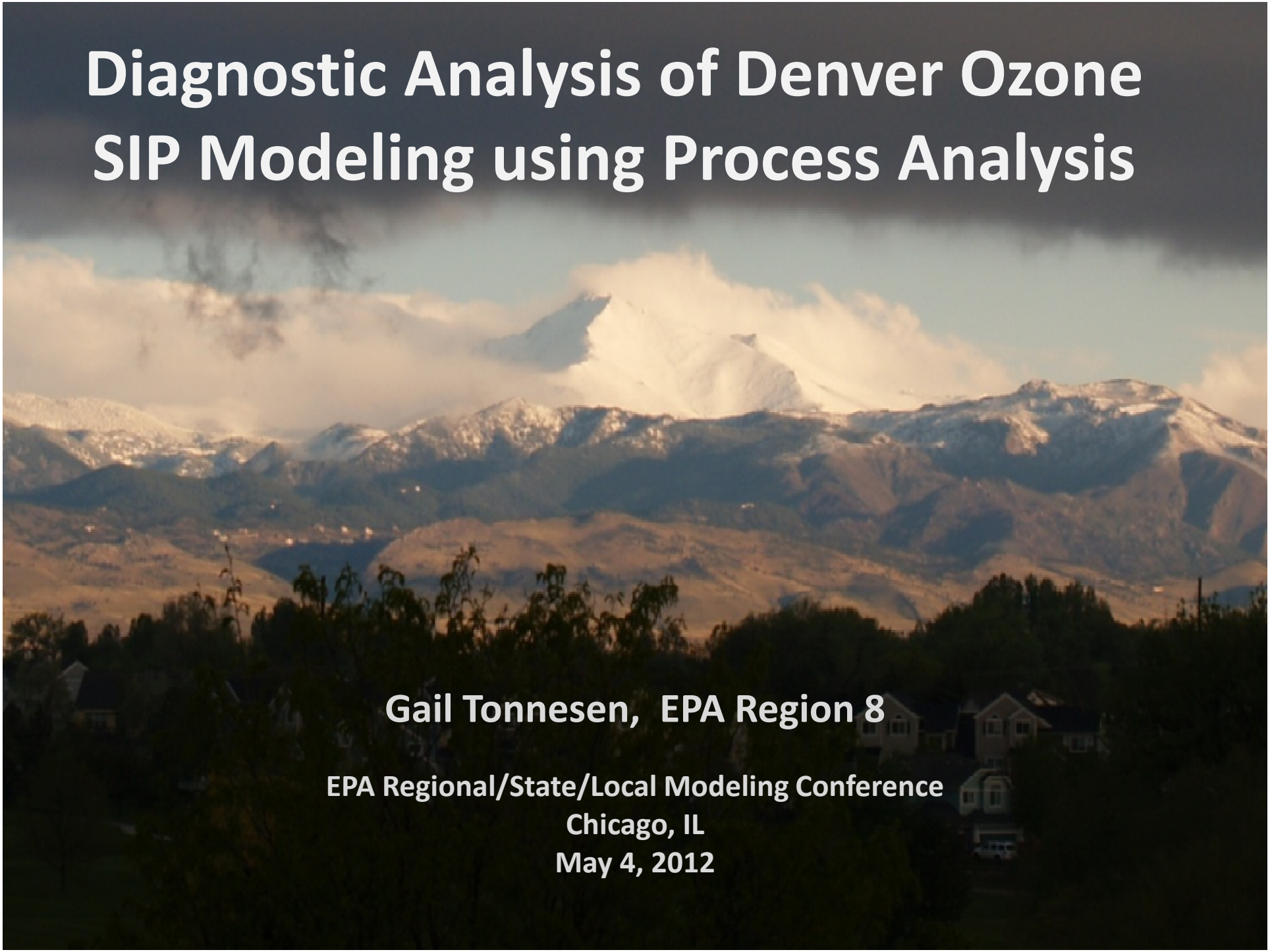
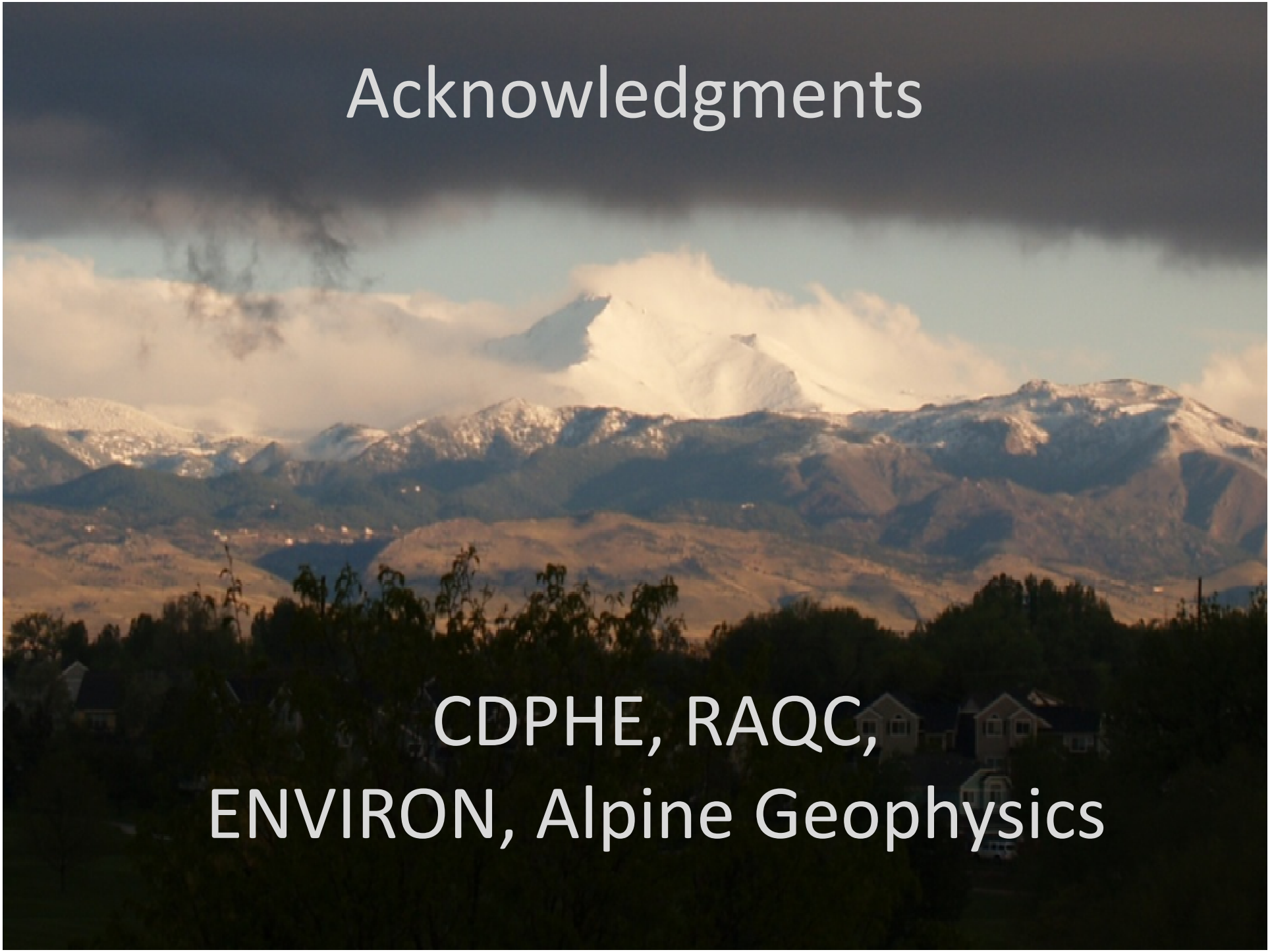
Diagnostic Analysis of Denver Ozone SIP Modeling using Process Analysis



Gail Tonnesen, EPA Region 8

EPA Regional/State/Local Modeling Conference
Chicago, IL
May 4, 2012



Acknowledgments

CDPHE, RAQC,
ENVIRON, Alpine Geophysics

Objectives

- Review of Chemical Process Analysis.
- Review of a 2006 episode used in the Denver ozone SIP modeling.
- Application of Chemical Process Analysis to July 15, 2006 ozone simulations using CMAQ and CAMx.

What is Process Analysis?

- Diagnostic tool designed to analyze individual physical processes and chemical reactions that determine pollutant concentrations:
  - Integrated Process Rates (IPR) include emissions, advection, dispersion, deposition and chemistry for selected model species.
  - Integrated reaction rates (IRR) hourly rate of each chemical reaction.
  - Chemical Process Analysis (CPA) pre-processing of IRR to evaluate chemical budgets of key species (including O3, Ox, radicals, NOy)

Chemical Process Analysis

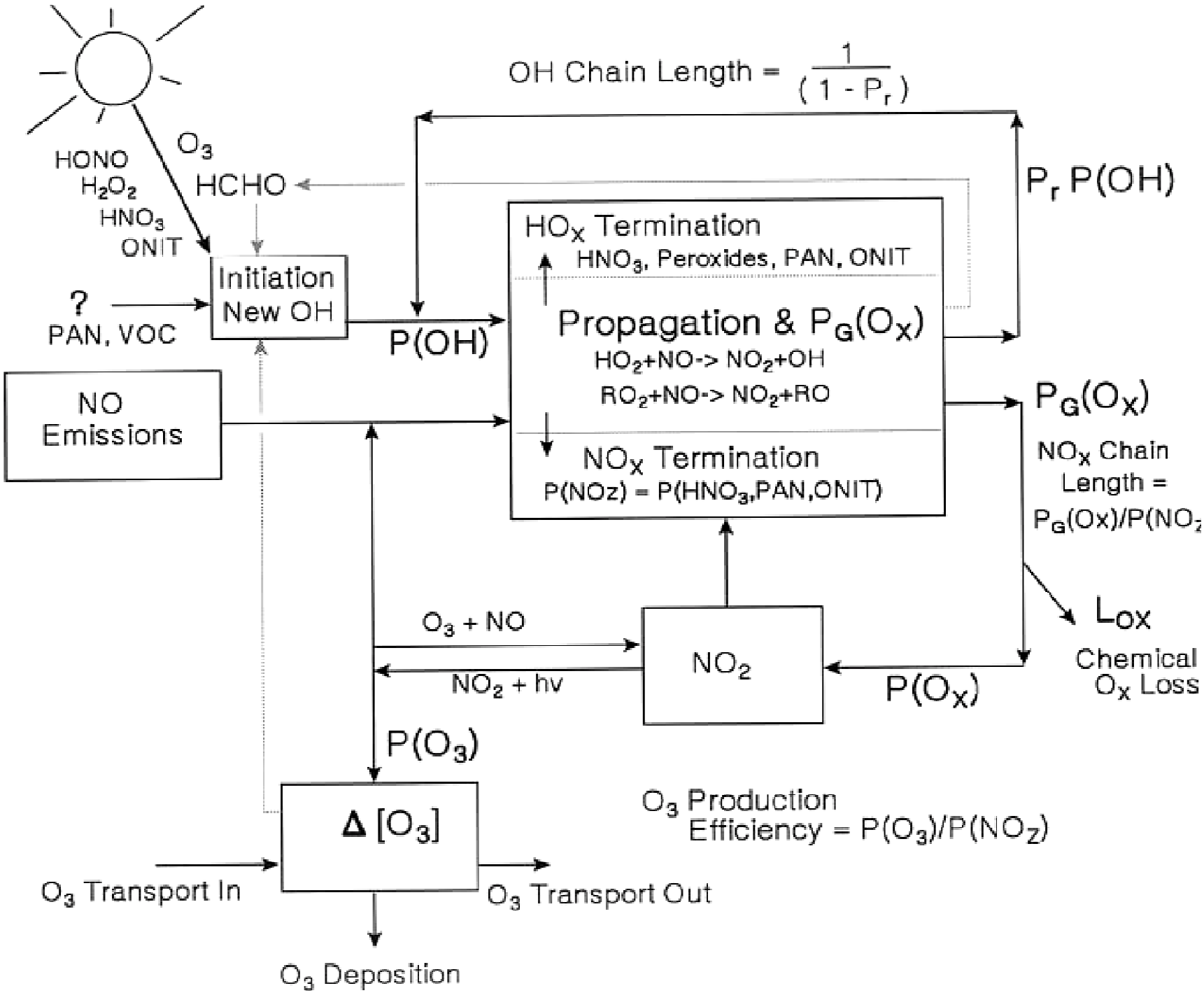
- O_3 formation occurs by the reactions HO_2+NO and RO_2+NO → NO_2
- For urban environments oxidation of NO emissions is a significant component of the system reactivity. Must consider sensitivity of total Ox to understand O3 sensitivity.

$$O_x = O_3 + NO_2 + PAN + HNO_3 + RNO_3 + \text{minor species}$$

$$PO_x = PO_3 + PNO_z \quad or, \quad PO_3 = PO_x - PNO_z$$

$$O_3 = \int PO_3 dt + O_{3\ initial} + O_{3\ transport} - O_{3\ deposition}$$

- Will evaluate both PO_x and PO_3
- Indicator ratio $PH_2O_2/PHNO_3$ can be used to assign PO_x and PO_3 to VOC sensitive or NOx sensitive regimes (similar to OSAT method).


OH Chain Length = 1 / (1 - Pr)
Pr P(OH)
O3
HCHO
HONO
H2O2
HNO3
ONIT
?
PAN, VOC
Initiation
New OH
P(OH)
HOx Termination
HNO3, Peroxides, PAN, ONIT
Propagation & PG(Ox)
HO2+NO-> NO2+OH
RO2+NO-> NO2+RO
NOx Termination
P(NOz) = P(HNO3,PAN,ONIT)
NO
Emissions
PG(Ox)
NOx Chain
Length =
PG(Ox)/P(NOz)
O3 + NO
NO2 + hv
NO2
P(Ox)
Lox
Chemical
Ox Loss
P(O3)
Δ [O3]
O3 Production
Efficiency = P(O3)/P(NOz)
O3 Transport In
O3 Transport Out
O3 Deposition

Source Code for CPA in CAMx

```
C...  { Net O3 Production }

      nn =  nn + 1
      ptname(nn)   = 'PO3_net'
      O3_prod =         R(  2)          ! O3P+O2=O3
     &         + 0.20 * R( 92)          ! C2O3+HO2=0.2*O3
     &         + 0.20 * R(108)          ! CXO3+HO2=0.2*O3
      PA(nn) = O3_prod - O3_loss

C...  { New HO2 from HCHO }

      nn = nn + 1
      ptname(nn)  = 'nwHO2_HCHO'
      PA(nn) = 2.*R(75)                ! FORM=2*HO2+CO
     &       +    R(77)                ! FORM+O=OH+HO2+CO
     &       +    R(78)                ! FORM+NO3=HNO3+HO2
```

Using CPA in CMAQ and CAMx

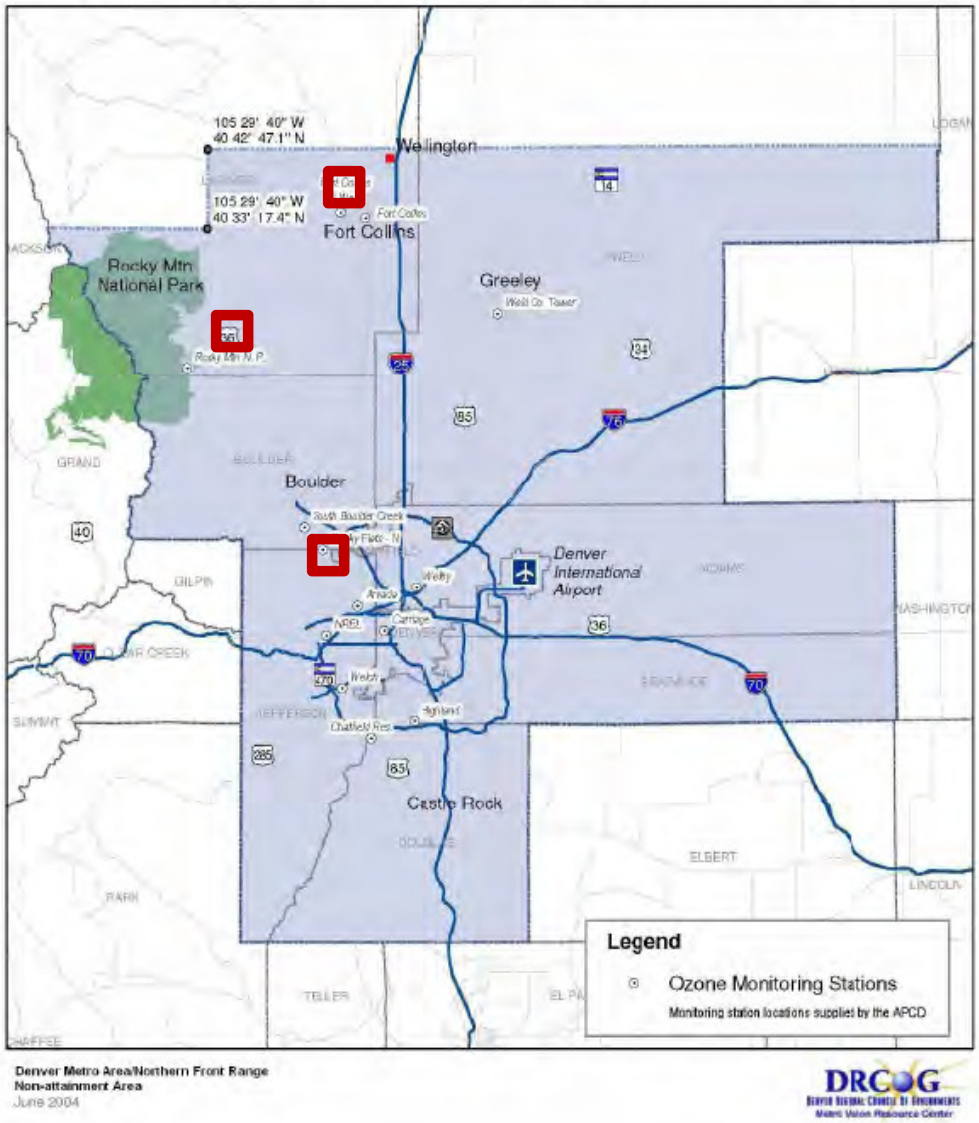
- CPA outputs files are in same format as concentration files and can be easily visualized along with model concentrations.
- Best to output 3-d CONC and CPA files to evaluate vertical mixing and transport.
- At a basic level, useful for QA of model simulations and for model comparisons.
- More effort required for volume based analysis :
  - Challenging to perform analysis of transported pollutants.

Comparison to DDM and OSAT

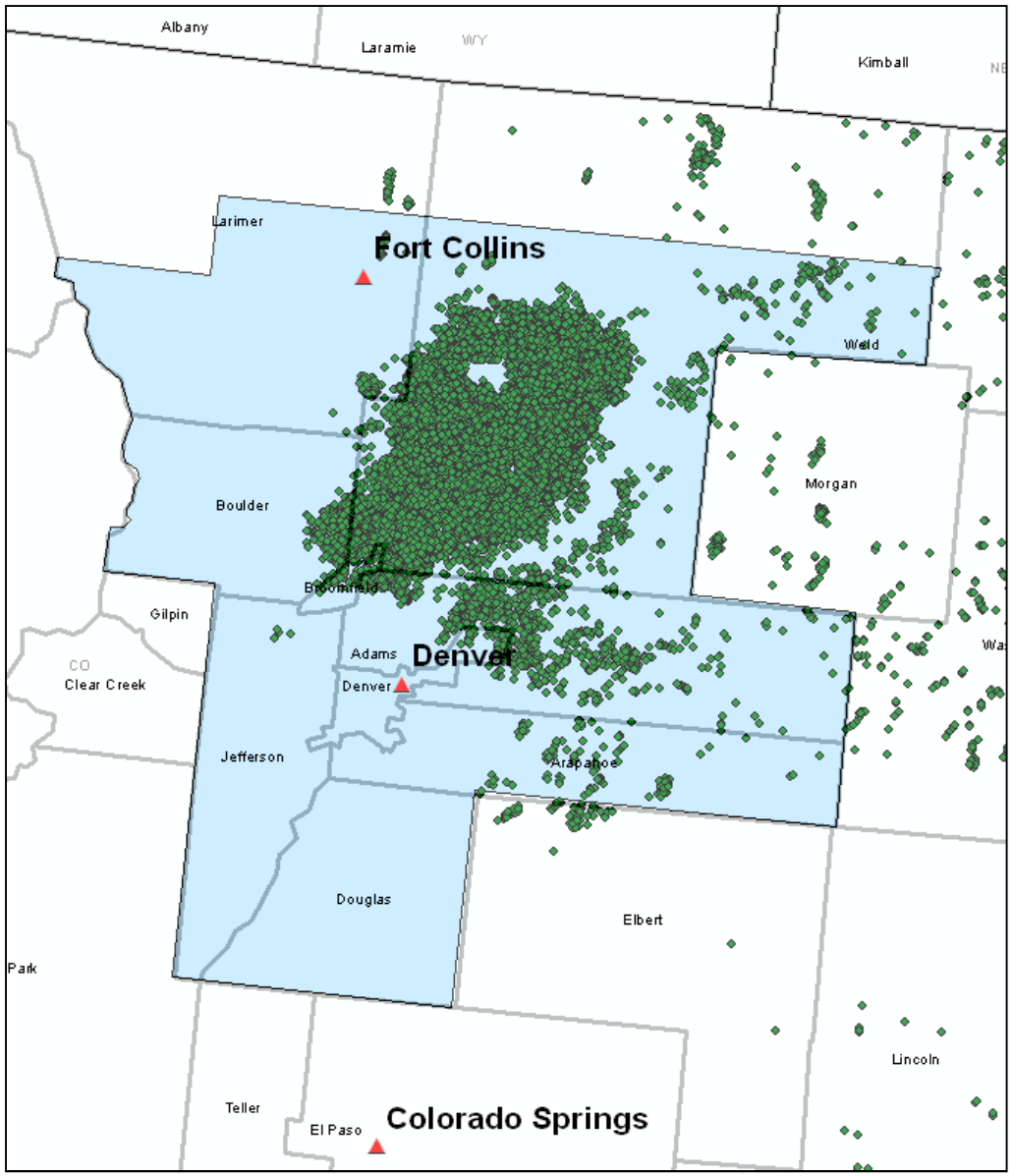
- DDM/sensitivity studies predict how ozone responds to changes at receptors.
- OSAT uses transported tracers to evaluate the sources that contribute to ozone at receptor sites.
- CPA evaluates the production of ozone and other chemical processes in the grid cells where it occurs.
  - CPA complement DDM and OSAT results.
  - CPA provides information on species budgets (Ox, HOx, NOx) that is not available from DDM and OSAT.

Denver Ozone Conceptual Model

- The Denver Front Range NAA includes monitors with exceedances in the Denver and Ft Collins areas.
- Typical urban emissions in Denver, Boulder, Ft Collins and Greeley, with oil and gas production emissions east of the urban areas in Weld County.
- Stagnant subsidence inversions with afternoon upslope flow west of the urban areas.
- High ozone aloft.

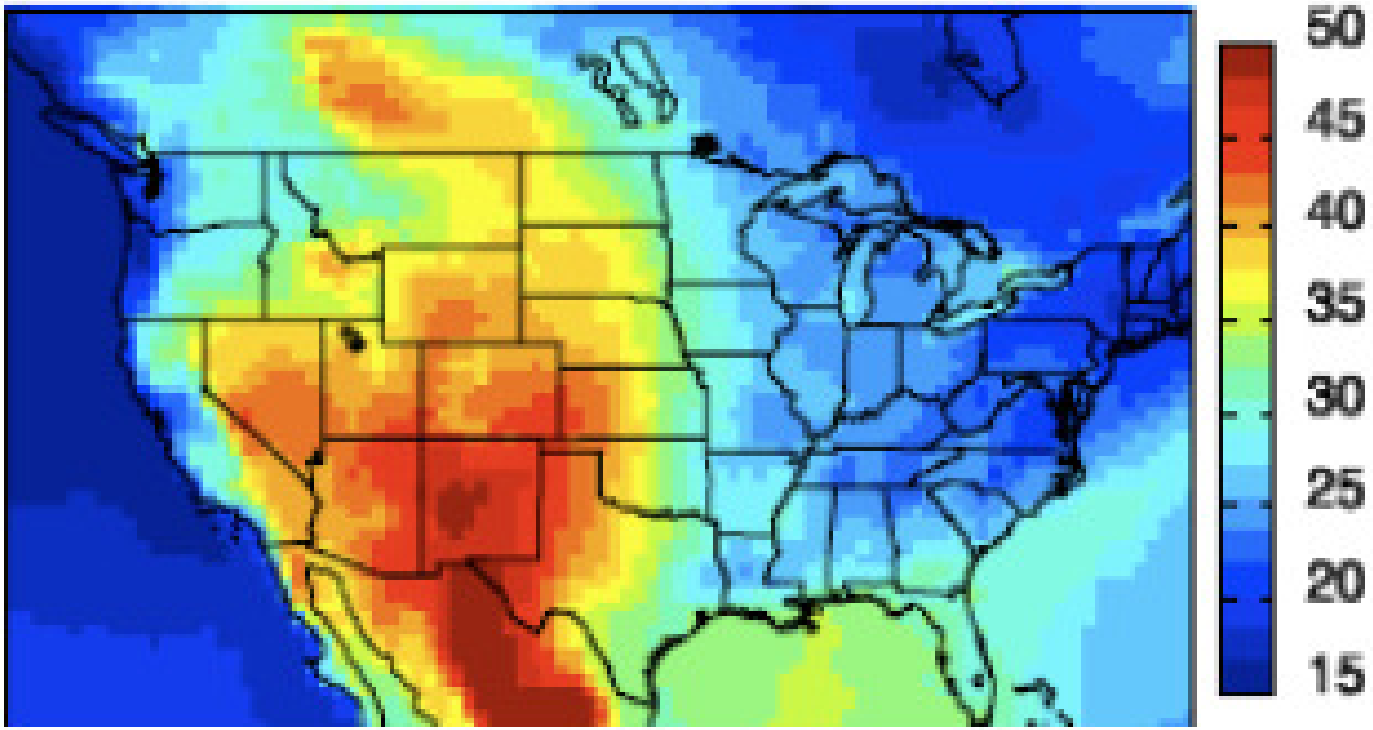


Location of Oil and Gas Wells in 2010



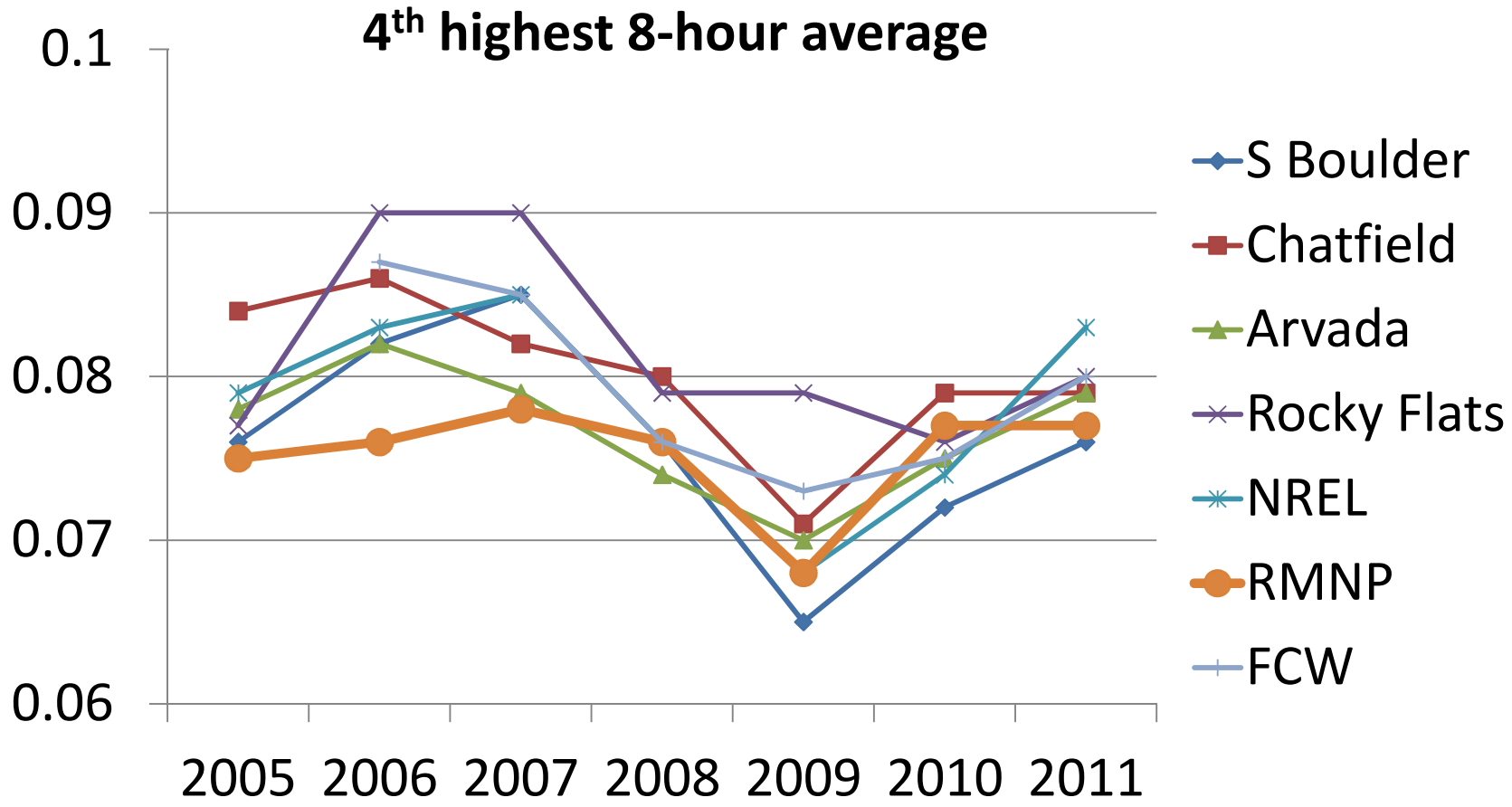
Background O3 in the West

- Global models predict high background O3 in the western states
- Consistent with high ozone concentrations at CASTnet sites.
- Background is variable and in the range of 40 to 60 ppb hourly.



GEOS-Chem predicted MD8 in summer 2006 with zero USA anthropogenic emissions, slide from Daniel Jacob presentation at 2011 PRB Workshop.

Ozone Trends in Denver/Front Range

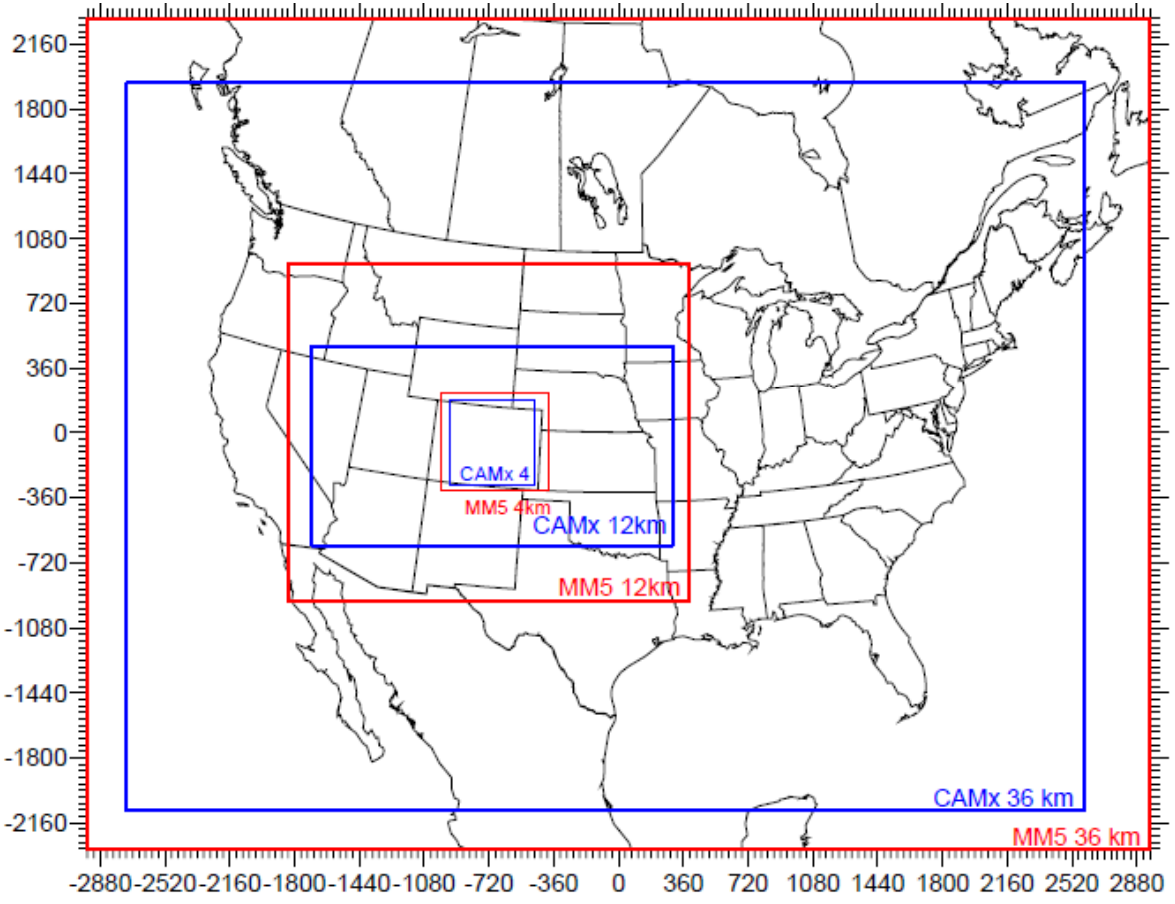


Possible explanations for low 2009 ozone concentration:

1. Unusually low temperatures in summer 2009.
2. Stratospheric O3 intrusion is correlated with El Nino/SO which affects jet stream patterns – Spring 2009 La Nina had low stratospheric ozone contribution and was a 15 year minimum in AM3 global model.

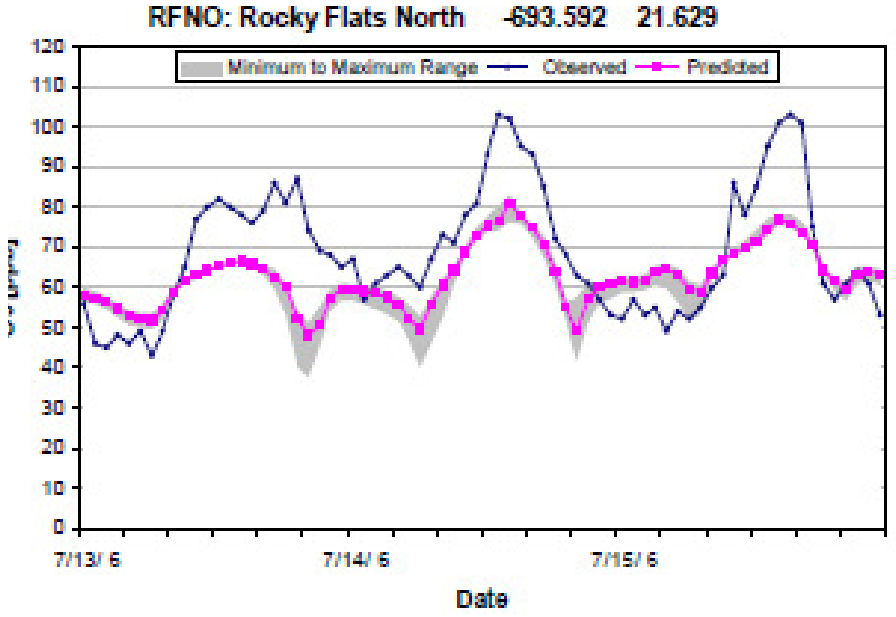
Modeling Domains

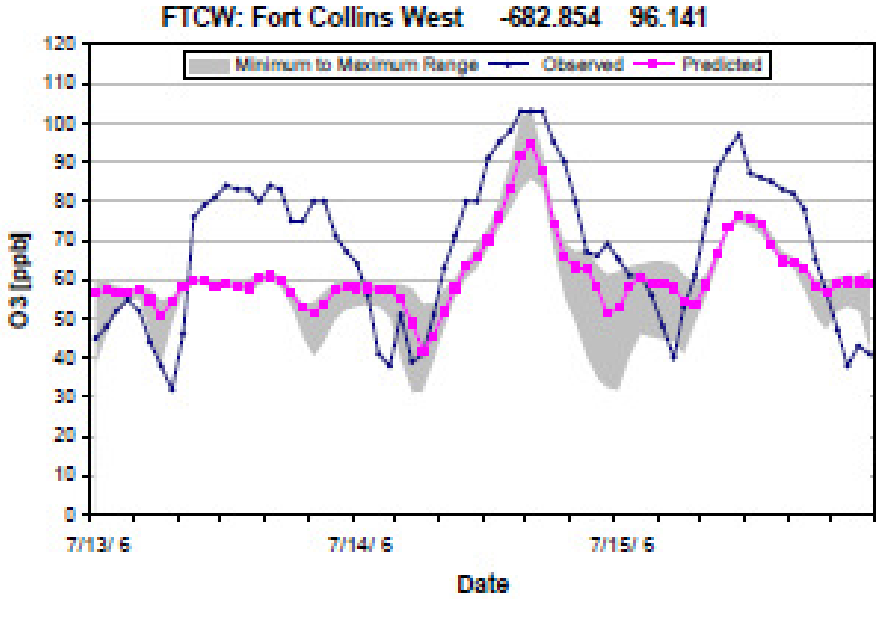
- 2006 episodic modeling completed by ENIRON/Alpine in 2008 using CAMx v4.5.
- 4 km high resolution grid 2-way nested in 12 km grid with BC from 36 km grid and GEOS-Chem.
- Updated modeling in progress using both CMAQ and CAMx for 2006 and 2008 episodes – preliminary model results shown here to illustrate the method.



Denver SIP July 13-15, 2006

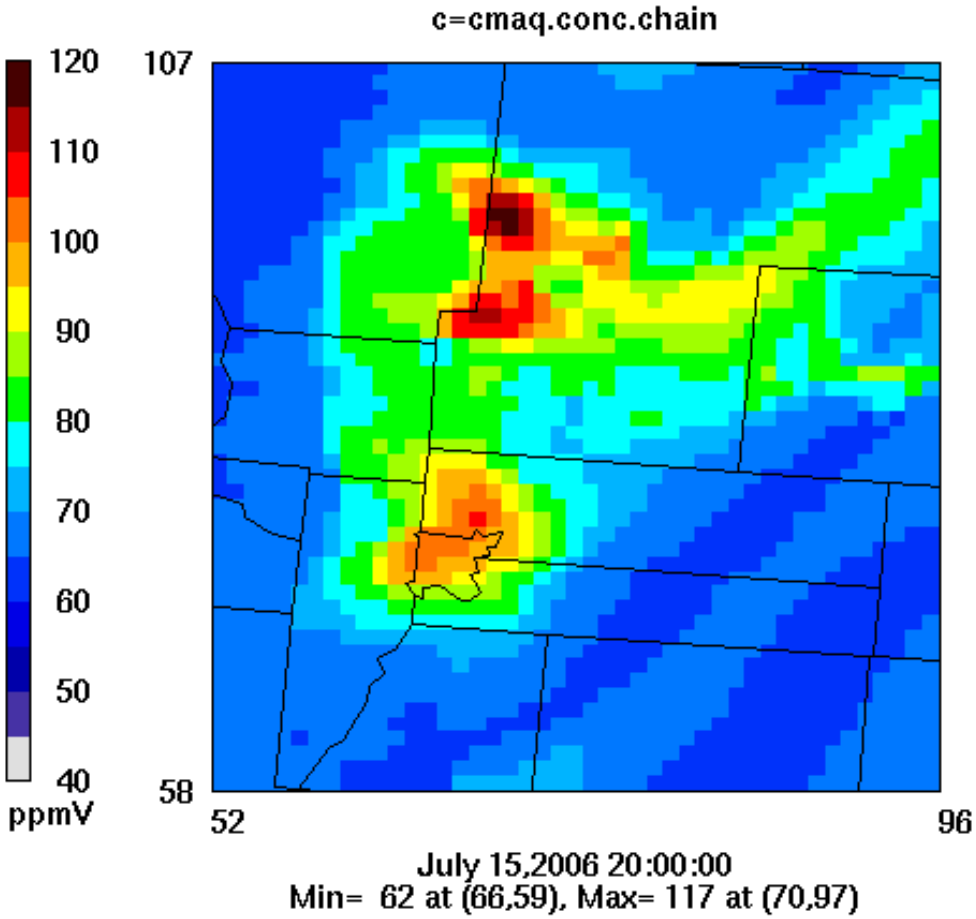
- Hourly maxima near 100 ppb on both days
- High ozone in Denver and Ft Collins areas.
- Application of Chemical Process Analysis to July 15, 2006 ozone simulations using CMAQ v4.7 & CAMx v5.4



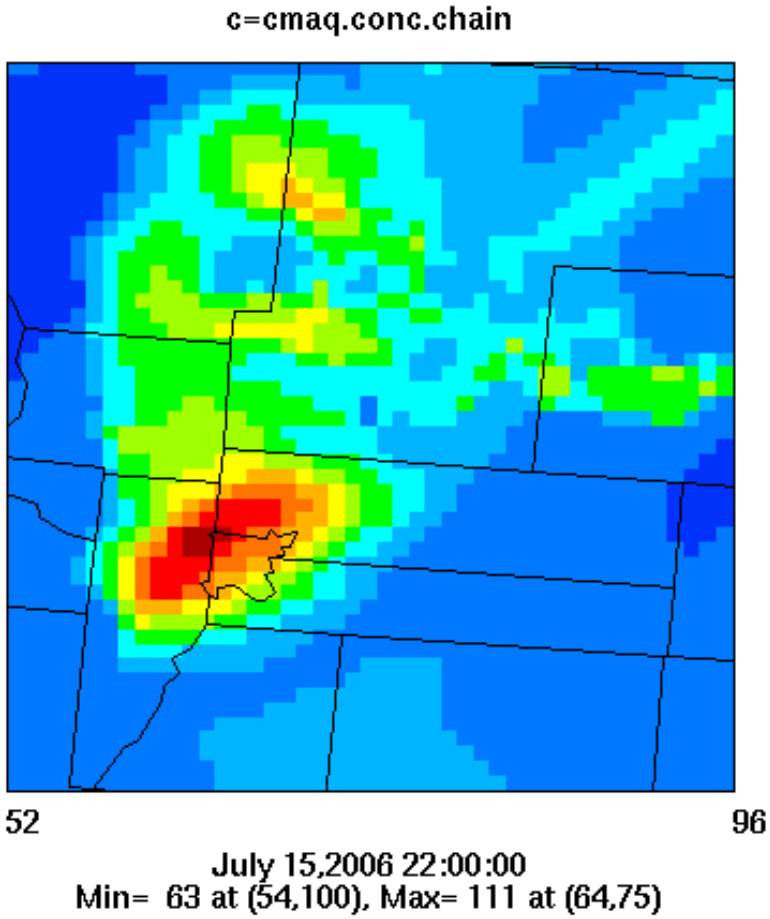


CMAQ model O3 on July 15

1 pm LDT

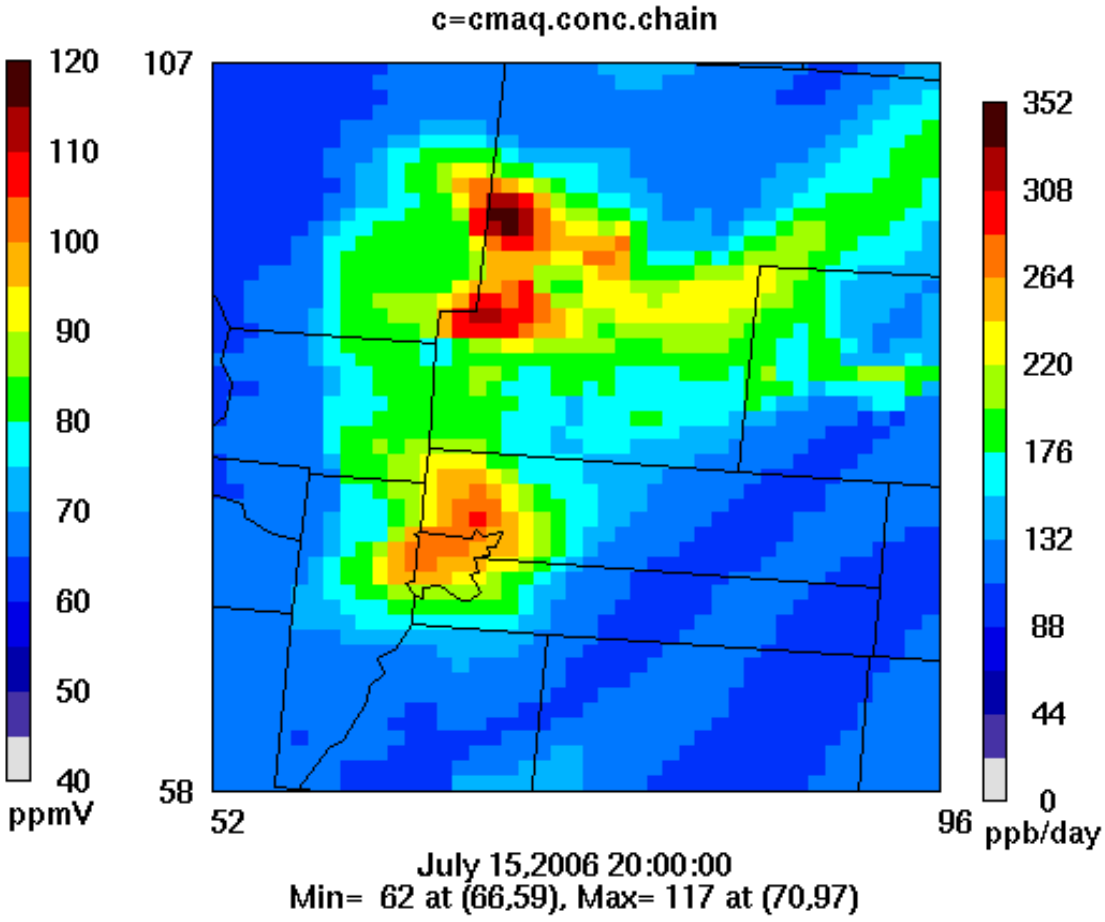


3 pm LDT



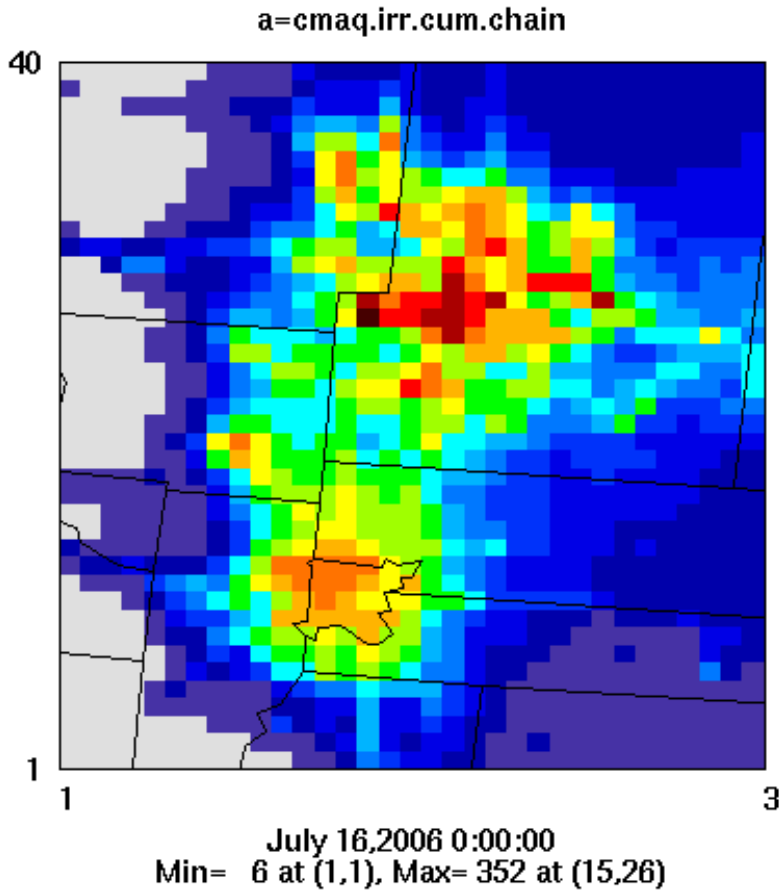
CMAQ model O3 and POx on July 15

1 pm LDT



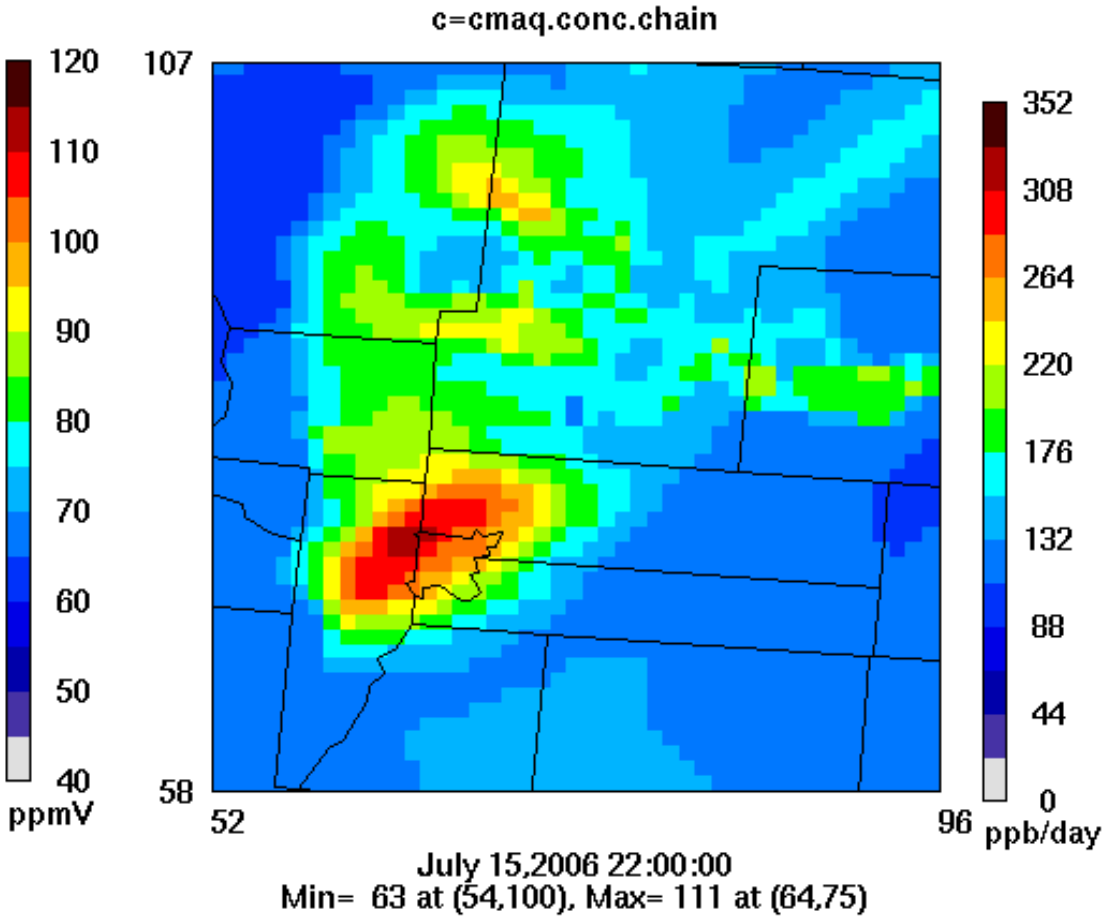
Lay 1 Ox Production

ppb/day



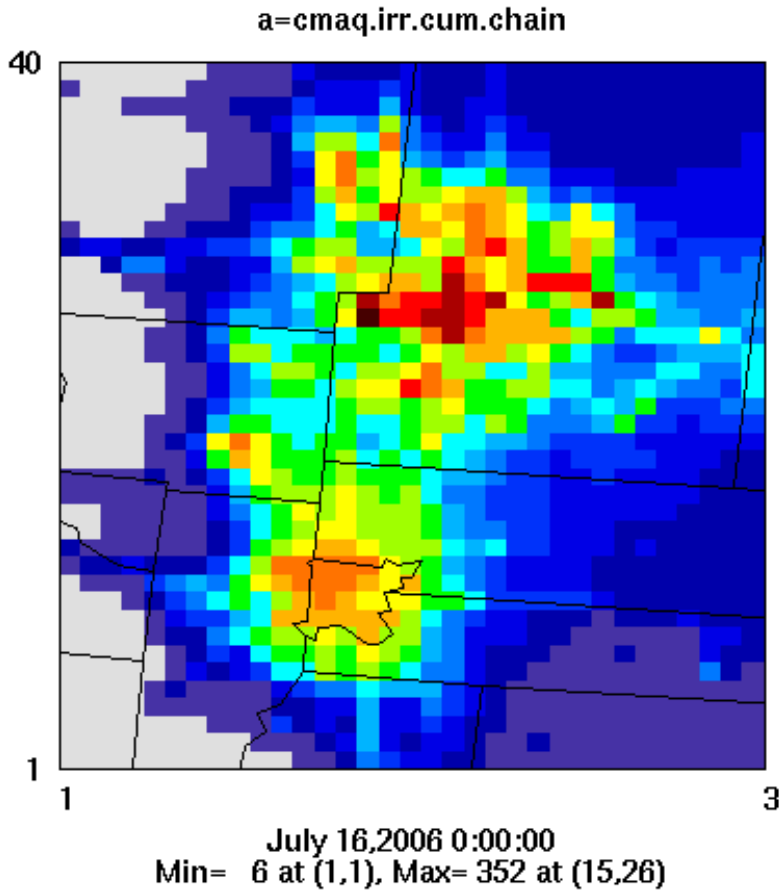
CMAQ model O3 and POx on July 15

3 pm LDT

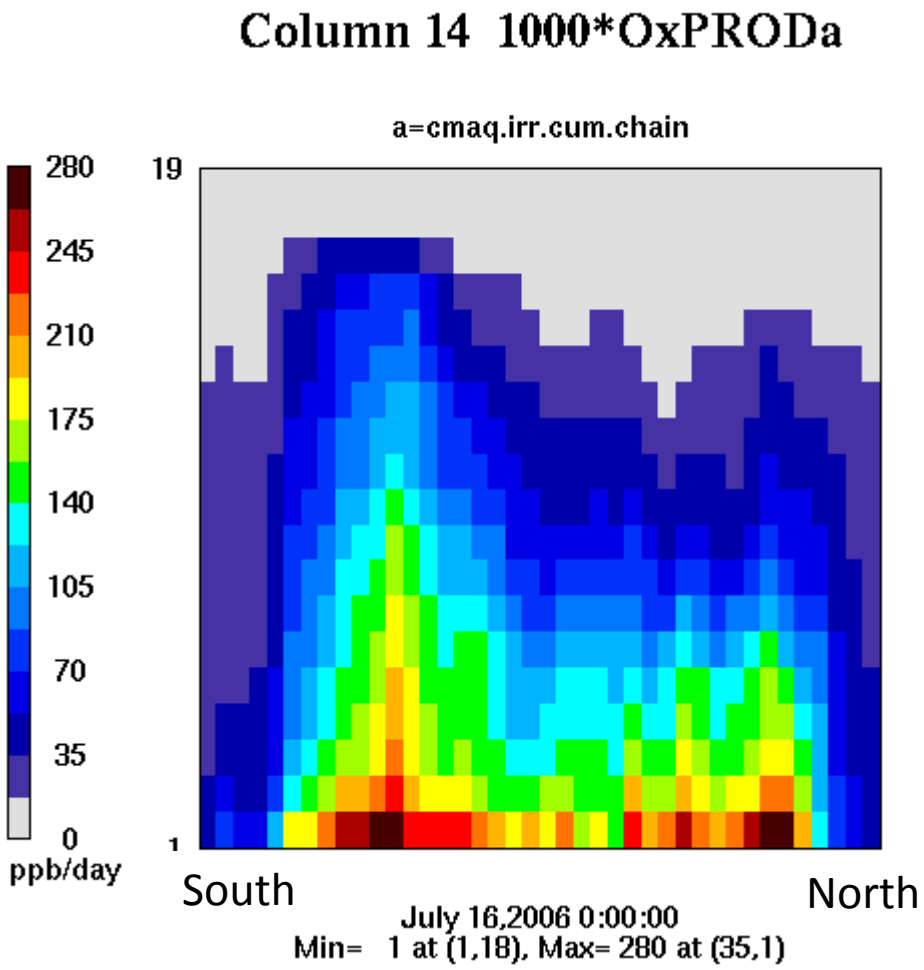


Lay 1 Ox Production

ppb/day



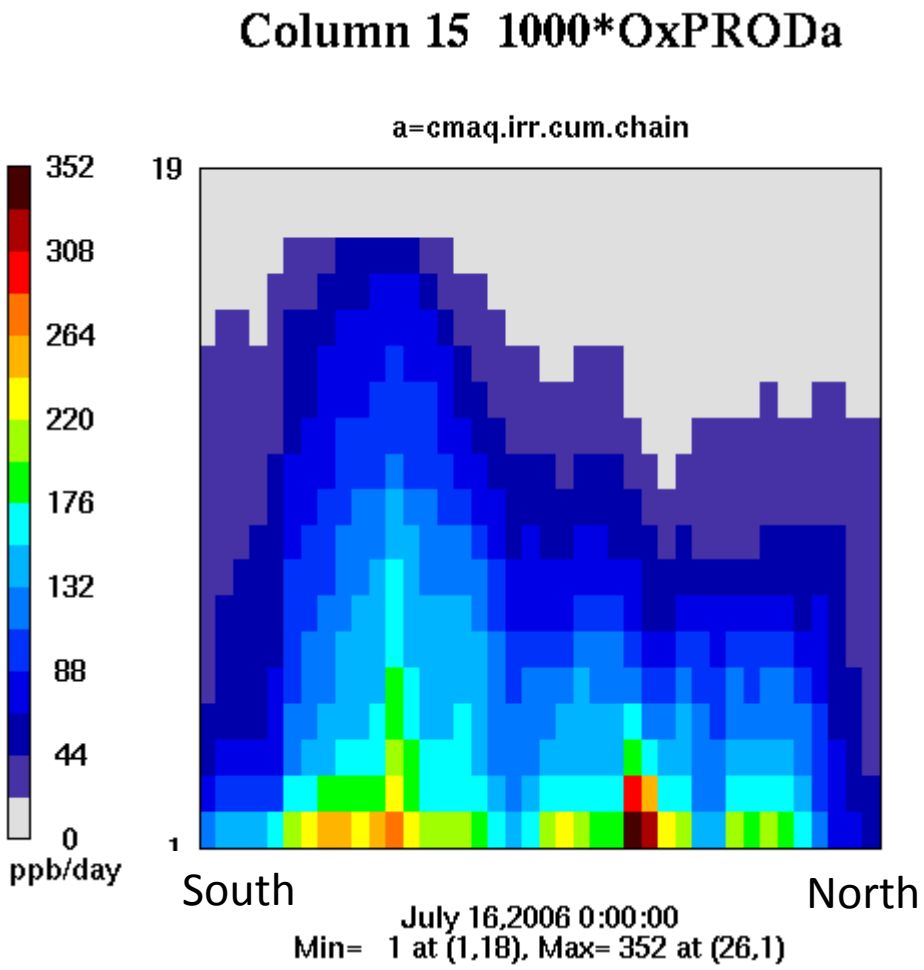
N-S Slice Col 14 (Denver) Ox Production



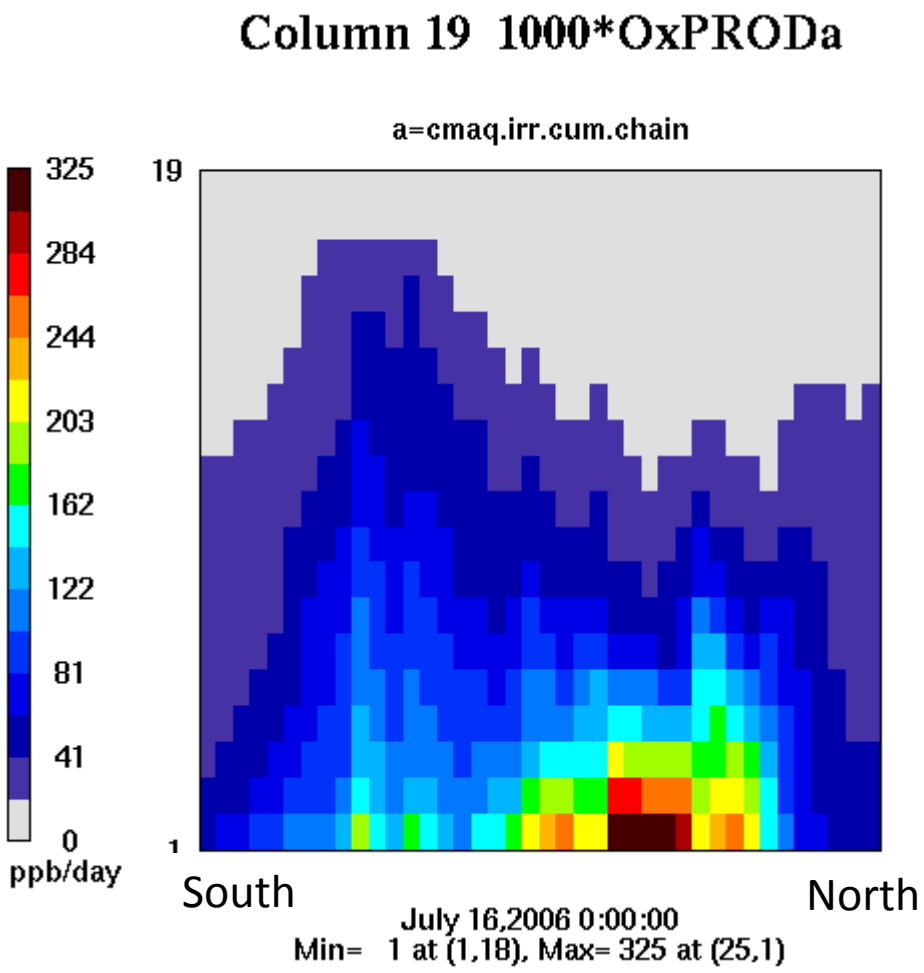
60% of weight factor in Ox production is layers 8 to 11.

Denver has larger Ox production in layers 8 to 11.

N-S Slice Col 15 (Denver) Ox Production



N-S Slice Col 19 (Weld Co.) Ox Production

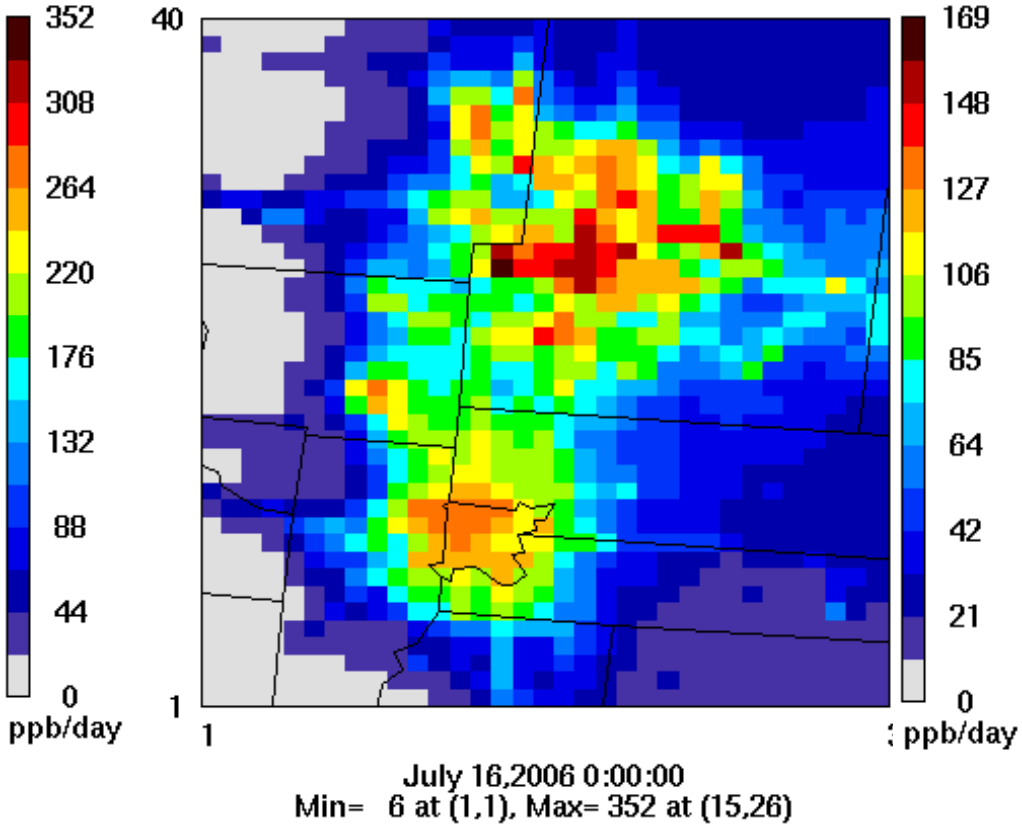


CMAQ Ox and O_3 Production

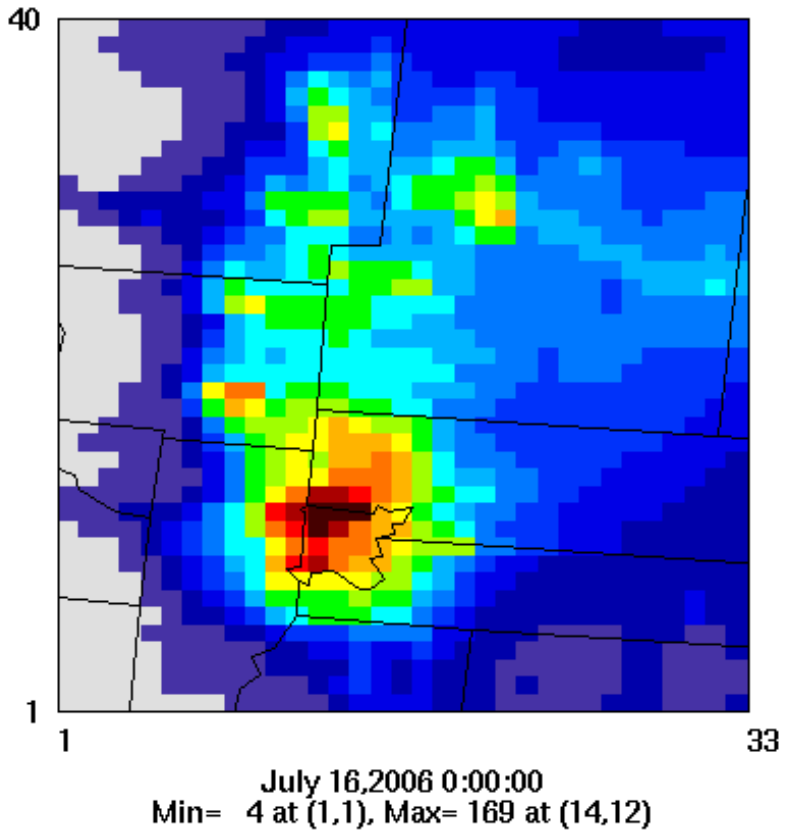
- Daily total Ox production on July 15, 2008
- Compare layer 1 to sum of first 11 layers:
  - Weight the layers by the product of layer depth and pressure.

P (mb)	CMAQ layer	height (m)	thickness	weight factor
877	11	1098	177	0.152
896	10	921	174	0.152
915	9	748	171	0.153
934	8	577	168	0.154
953	7	409	83	0.077
962	6	326	82	0.078
972	5	243	82	0.078
981	4	162	65	0.062
989	3	97	40	0.039
993	2	56	32	0.031
997	1	24	24	0.024

Layer 1 Ox Production

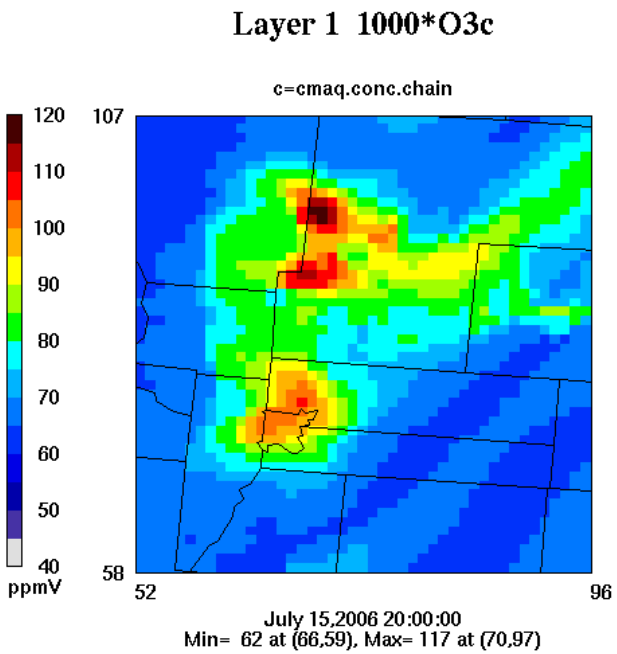


Sum Layer 1 to 11 Ox Prod

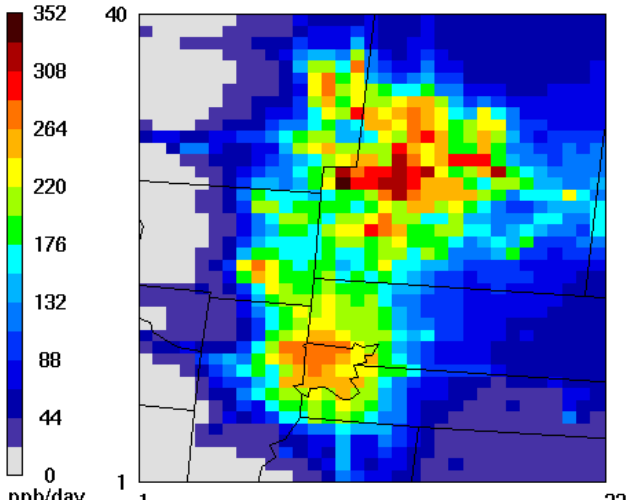


Layer 1 plot indicate large Ox production in Weld Co, consistent with high surface ozone in western Weld Co. at 1 pm. There is less Ox prod in upper layers in Weld Co. and low O3 concentration in layer 10 in Weld Co. Sum of layer 1-11 Ox production does not accurately represent surface contributions to Weld Co. ozone at 1 pm.

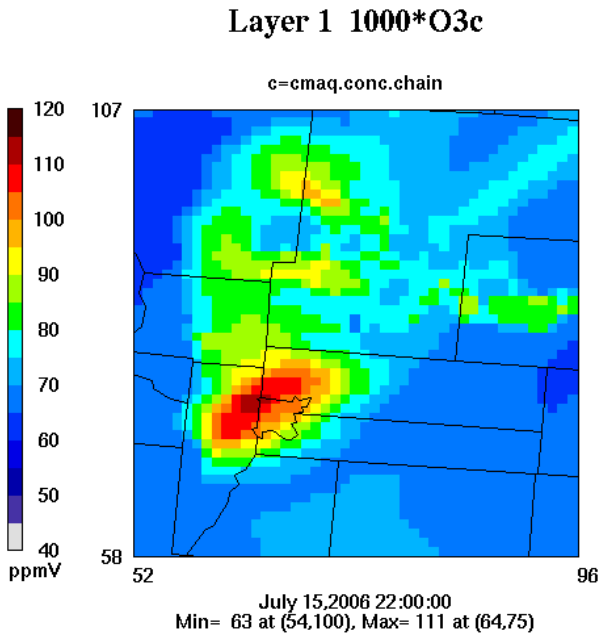
1 pm LDT



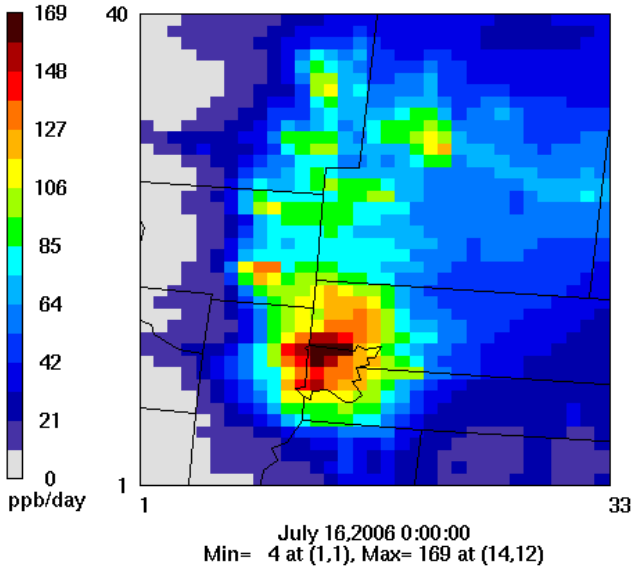
Layer 1 Ox Production



3 pm LDT

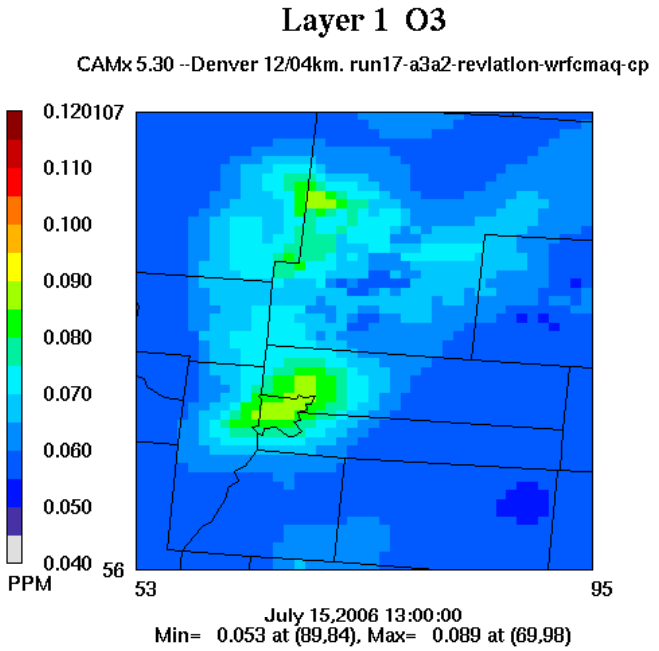


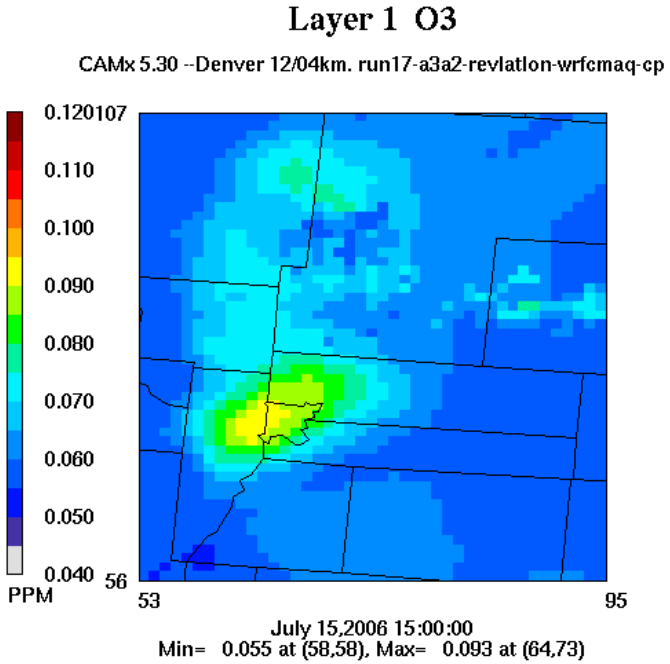
Sum Layer 1 to 11 Ox Prod



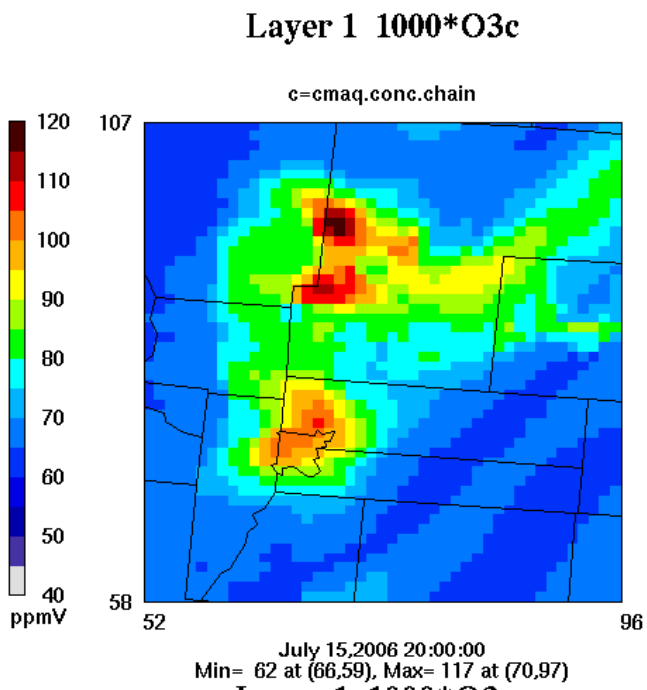
Appears to be rapid vertical mixing in western Weld Co between 1 pm and 3 pm, resulting in lower surface ozone levels (see next slide comparing 1 pm and 3 pm). By 3 pm the sum of Ox Prod in layers 1 to 11 better represents surface ozone levels.

CAMx

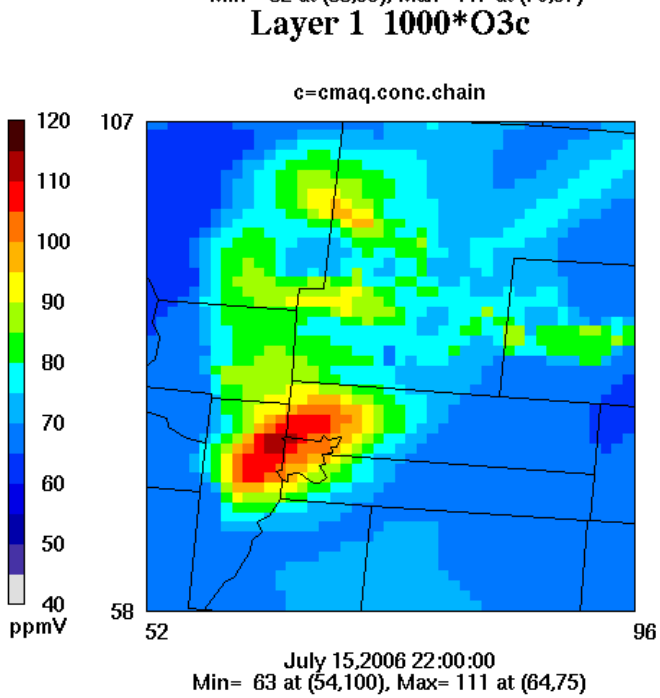




CMAQ

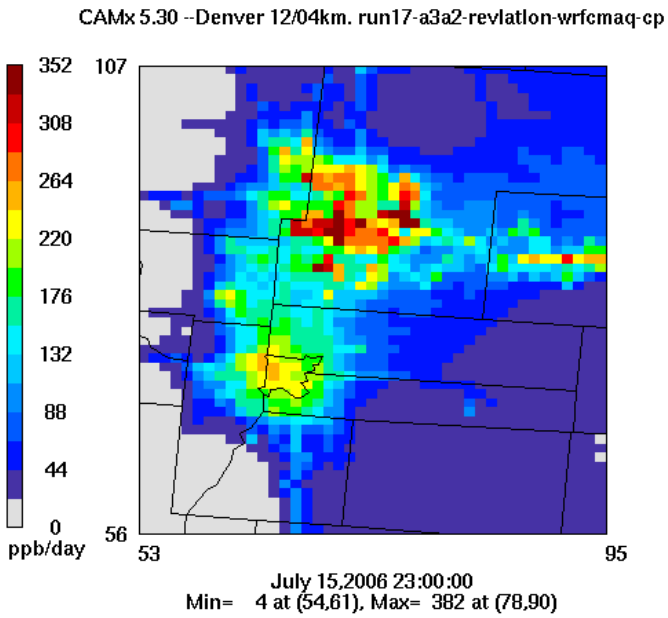


1 pm LDT

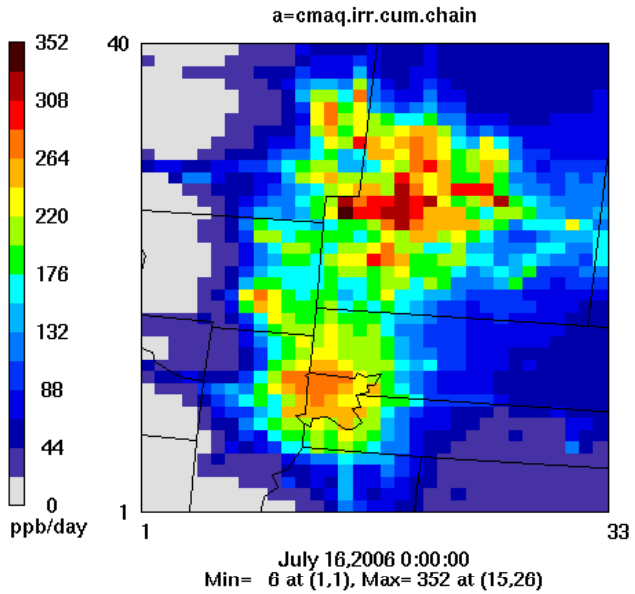


3 pm LDT

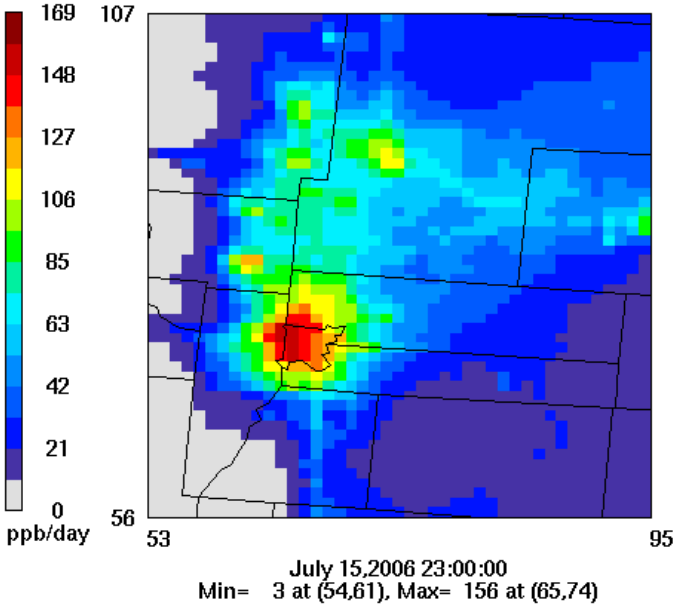
CAMx Ox Prod Layer 1



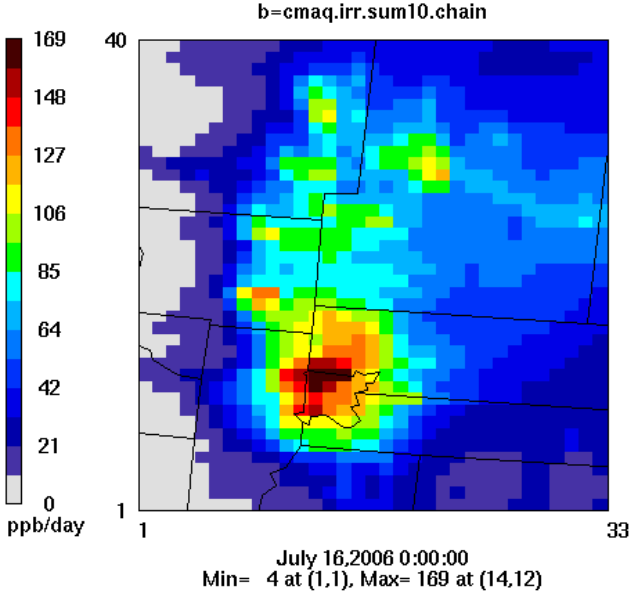
CMAQ Ox Prod Layer 1



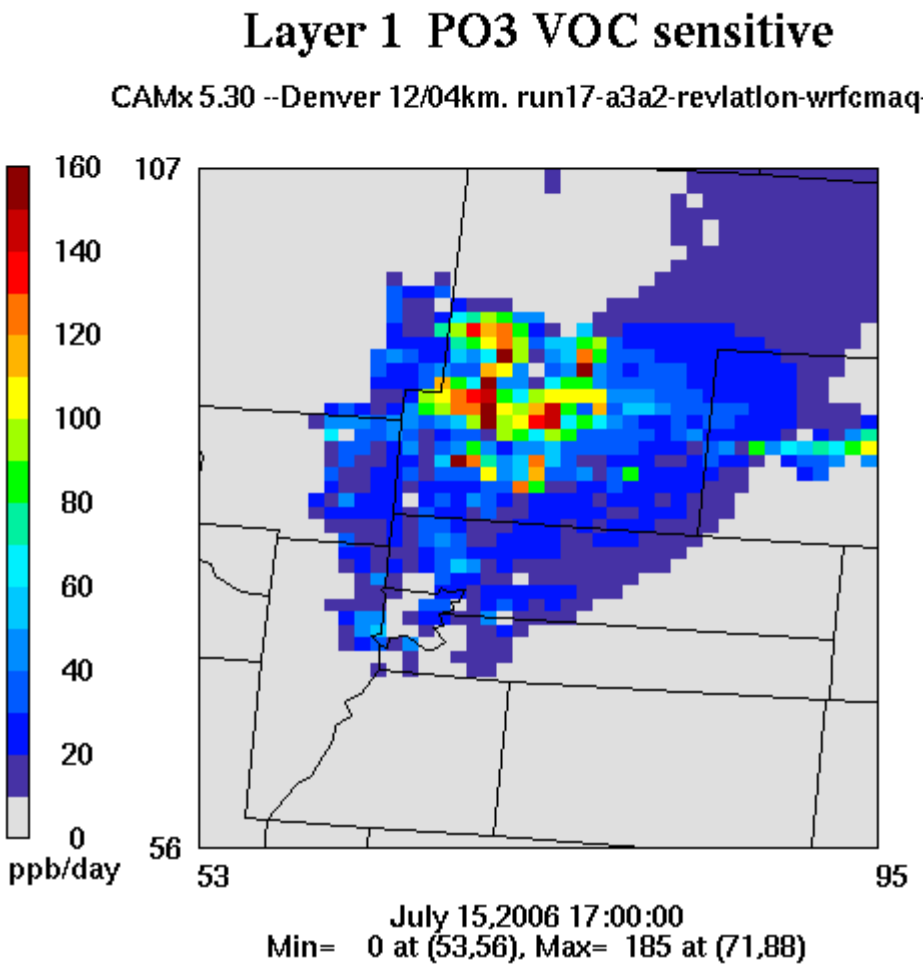
CAMx Ox Prod Sum Layers 1 to 11

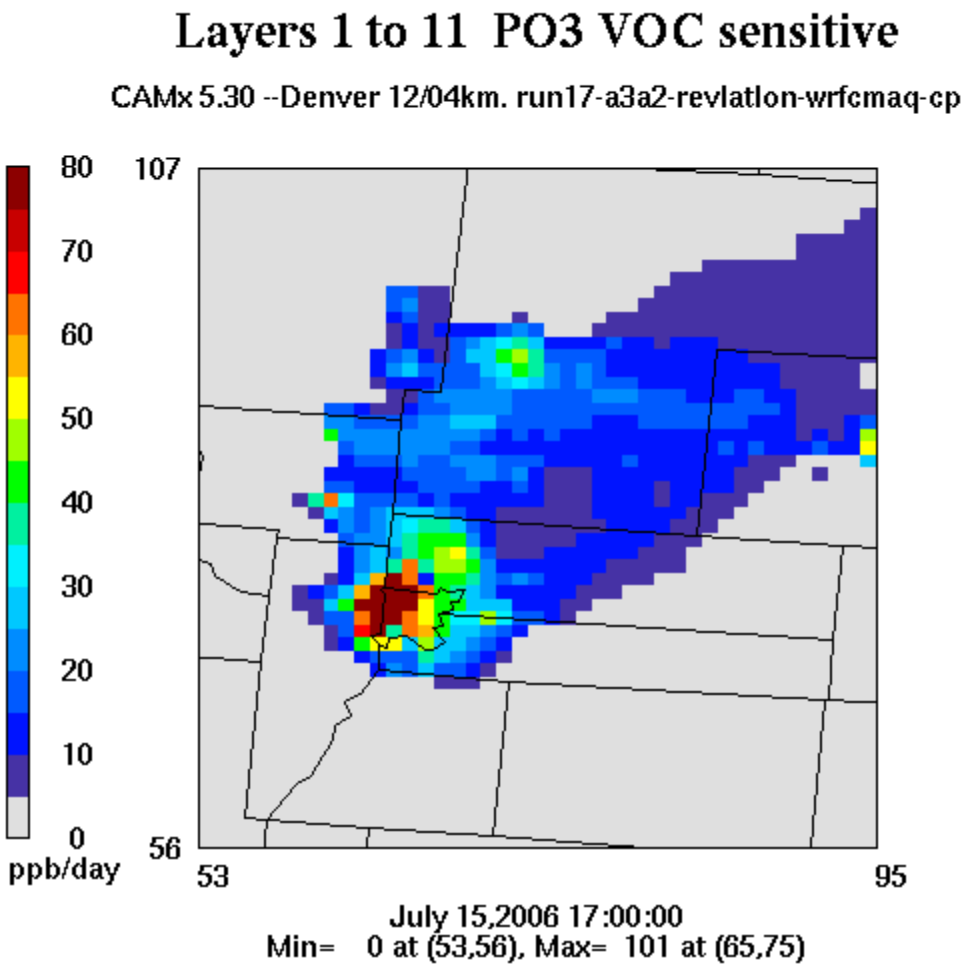


CMAQ Ox Prod Sum Layers 1 to 11

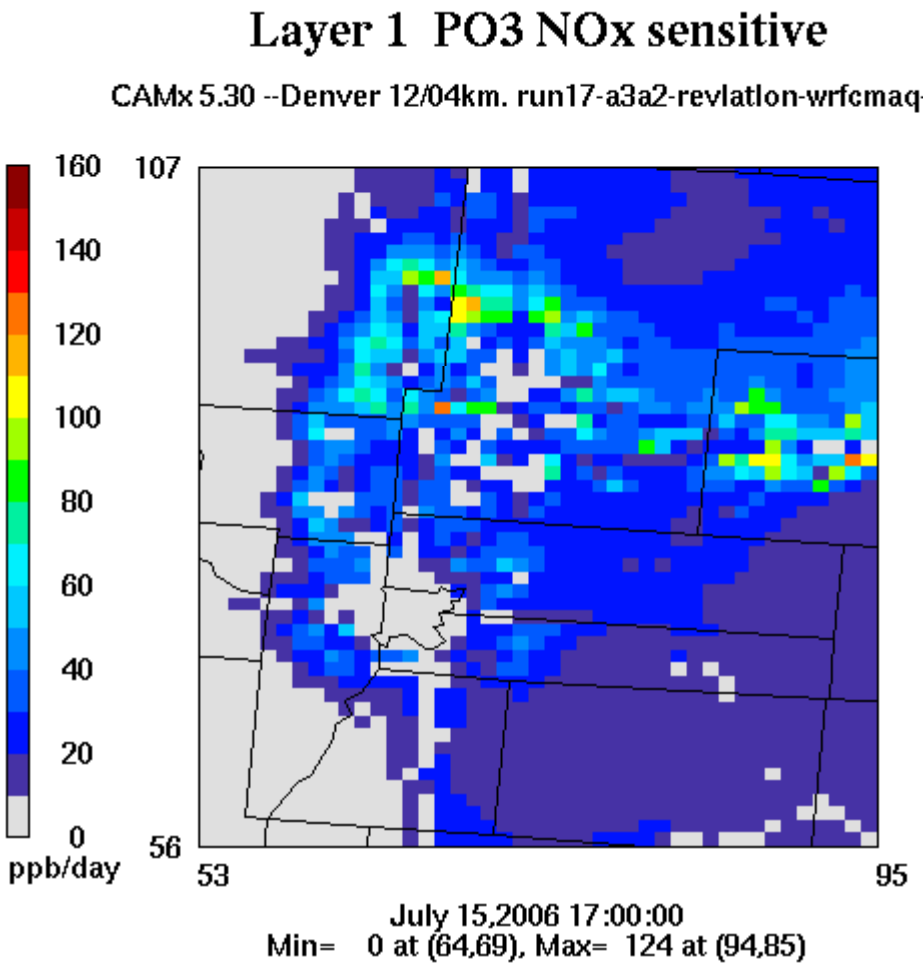


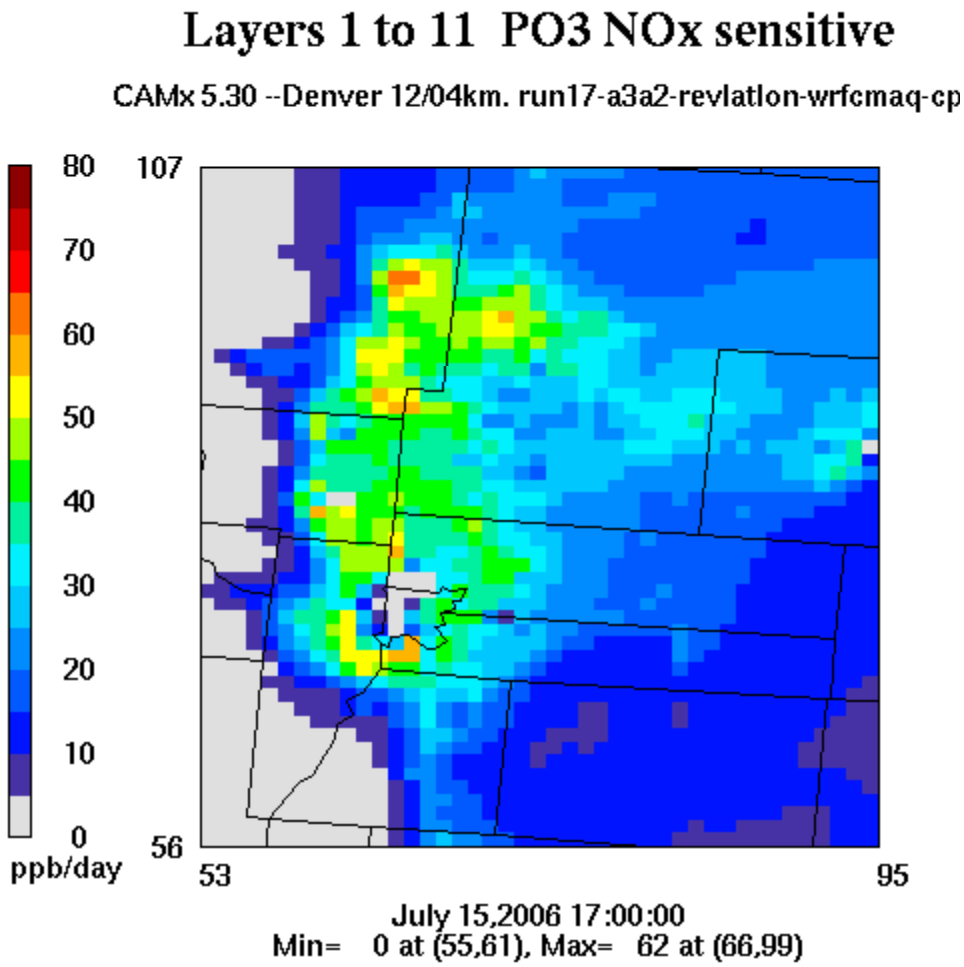
Comparison of O3 production in VOC sensitive regime for layer 1 and the weighted sum of layers 1 to 11: Net PO3 is negative or small for layer 1 in the Denver area (also need to look at Ox production there). There is large PO3 in VOC sensitive regime in Weld county layer 1. After summing layers, the Denver area has large PO3 in VOC sensitive regime. In Weld county PO3 is large near the surface but smaller aloft.



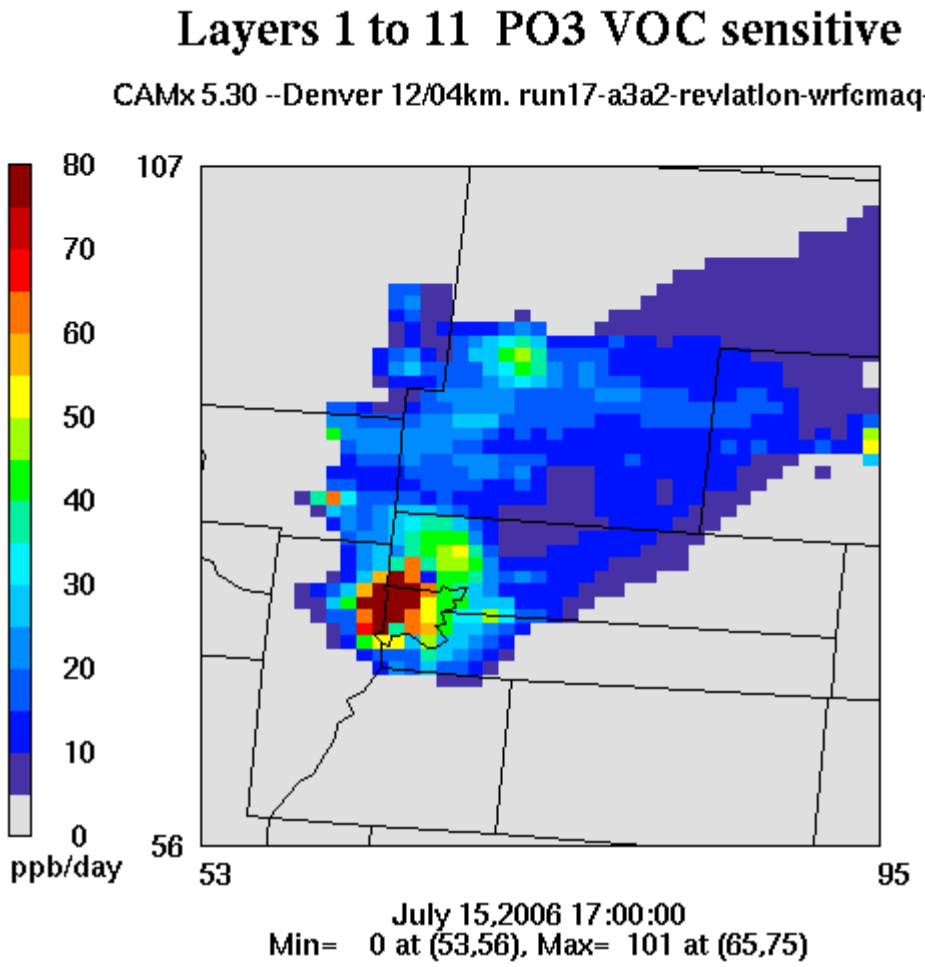


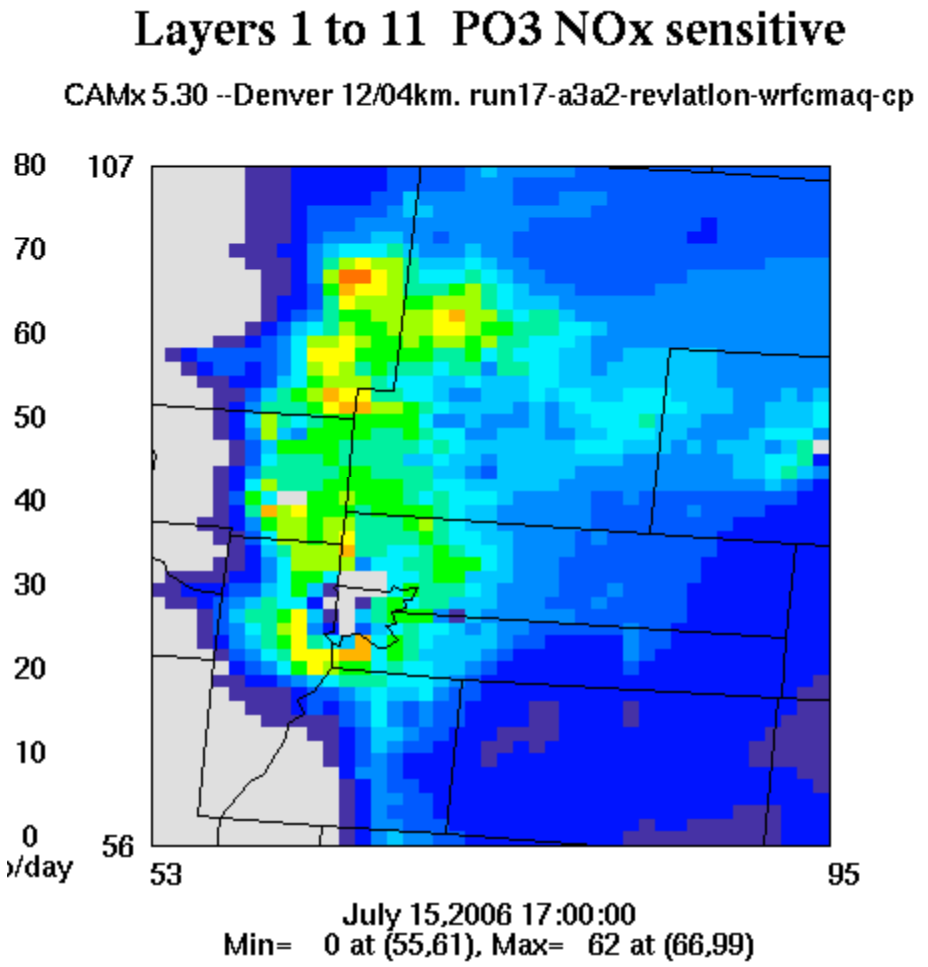
Comparison of O3 production in NOx sensitive regime for layer 1 and the weighted sum of layers 1 to 11: Results indicate that PO3 is VOC sensitive and radical limited in Denver, Boulder and central Weld county. PO3 is NOx sensitive in Ft Collins, Loveland, Greely and suburban Denver.



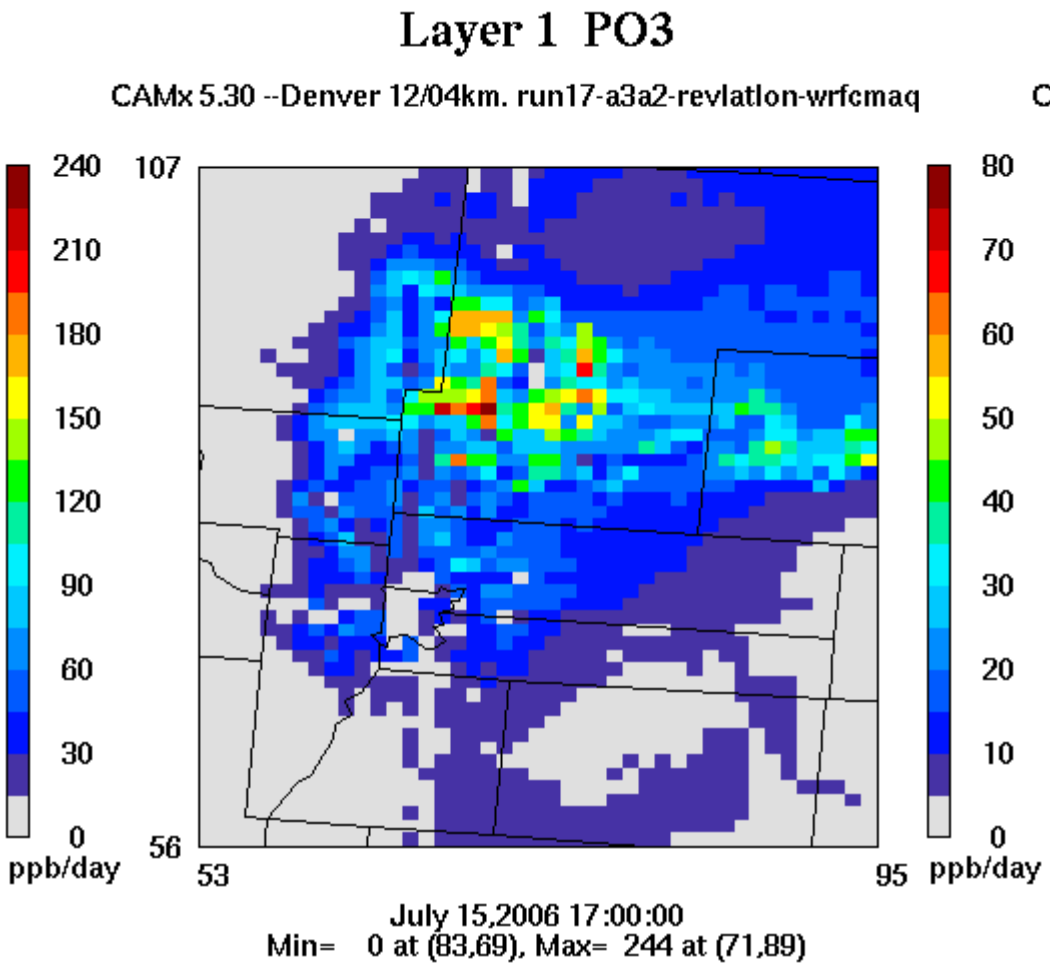


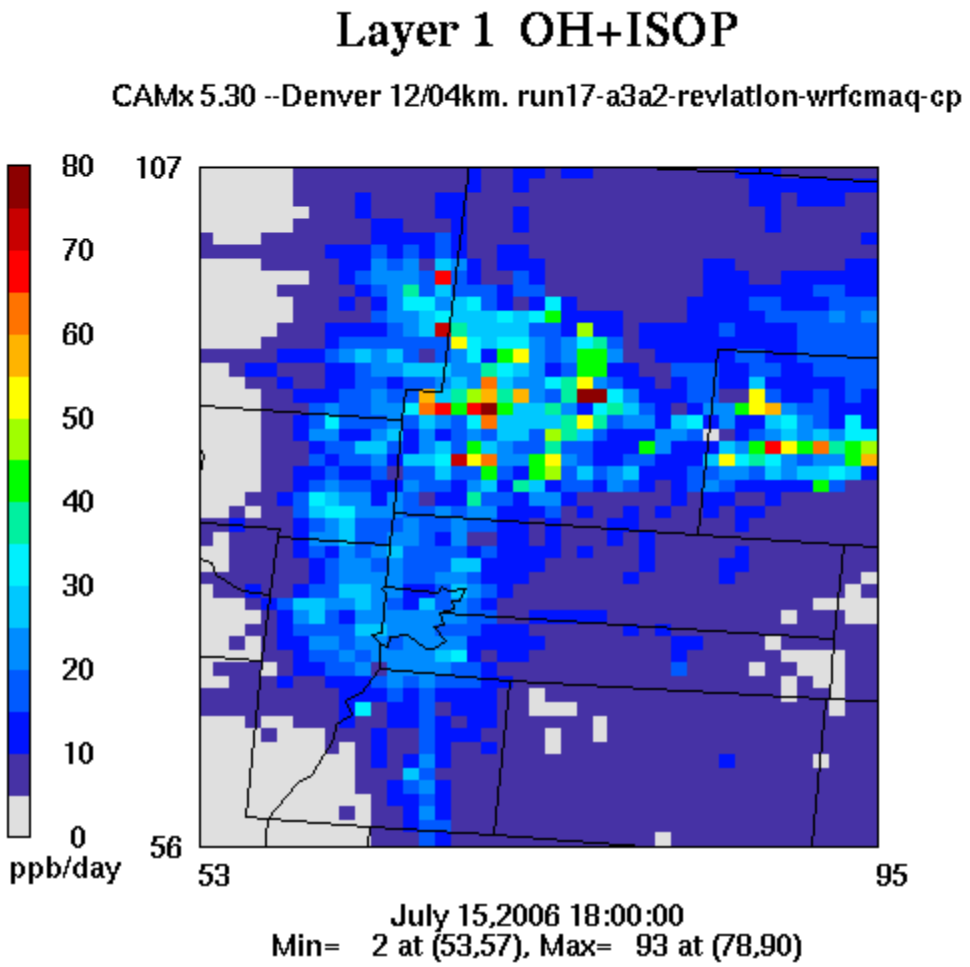
Comparison of O3 production in layers 1 to 11 for VOC and NOx sensitive regimes.





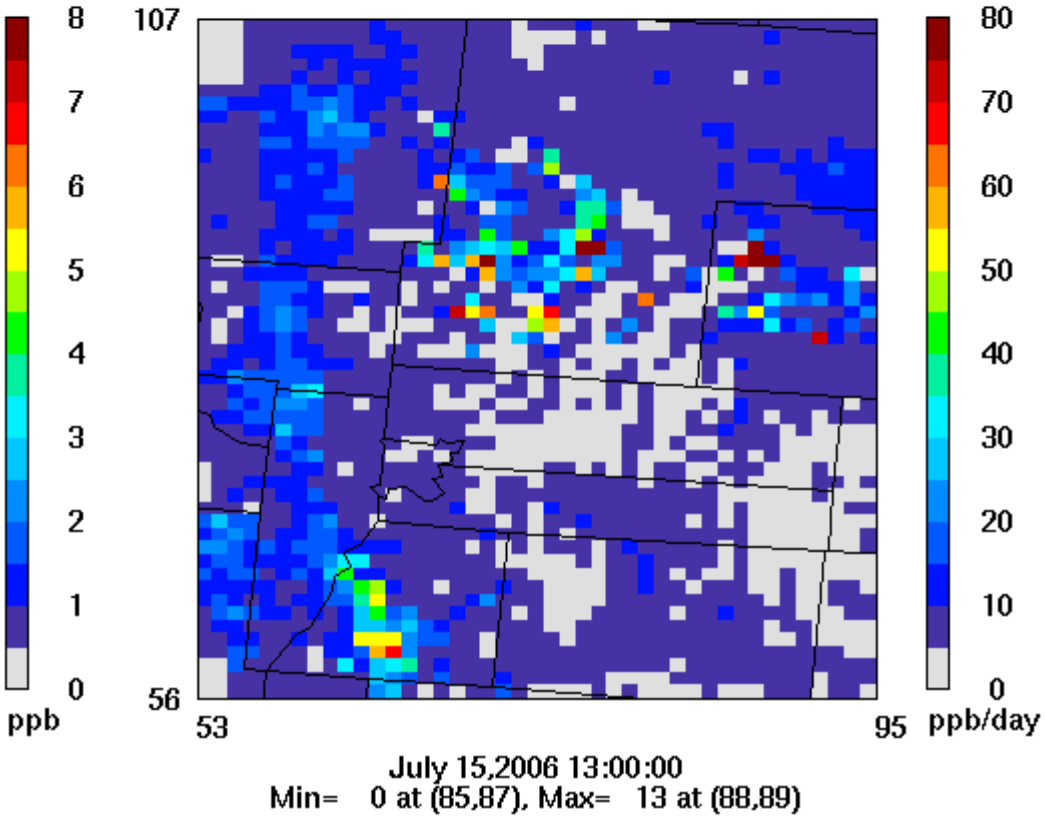
Comparison of layer 1 PO3 and OH+ISOP indicates that much of the surface layer PO3 in Weld county is a result of isoprene emissions.



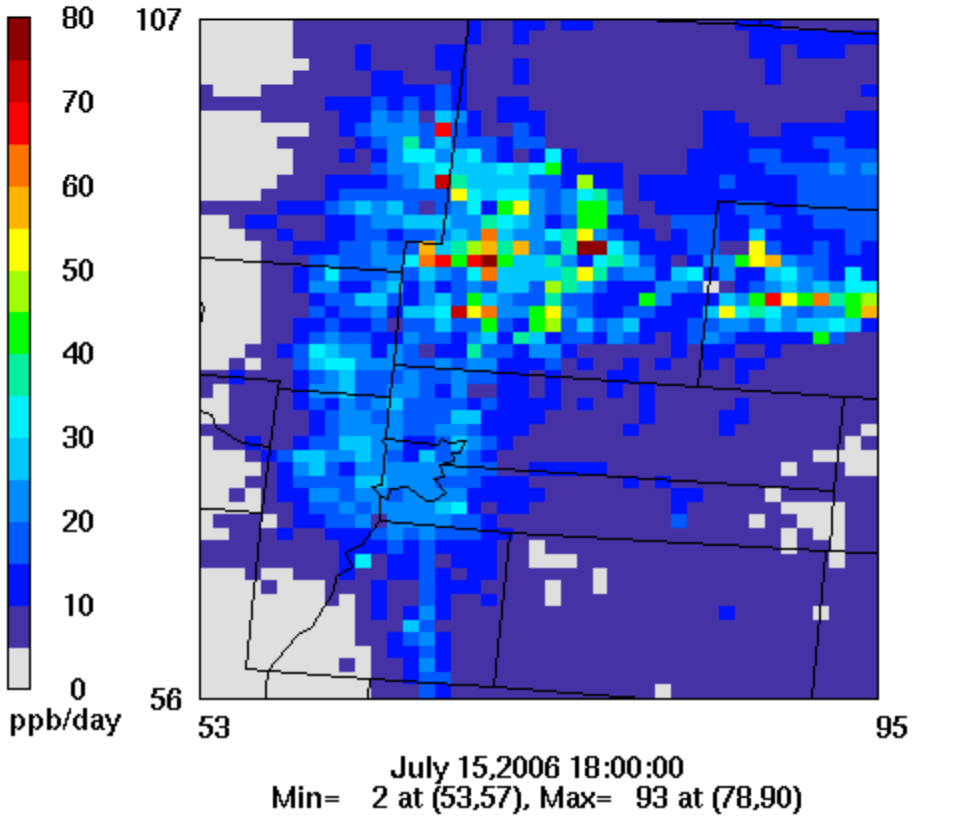


High isoprene concentrations a 1 PM LDT and large reacted with OH in Weld county in Layer 1, is isoprene from agriculture or from trees in river valley?

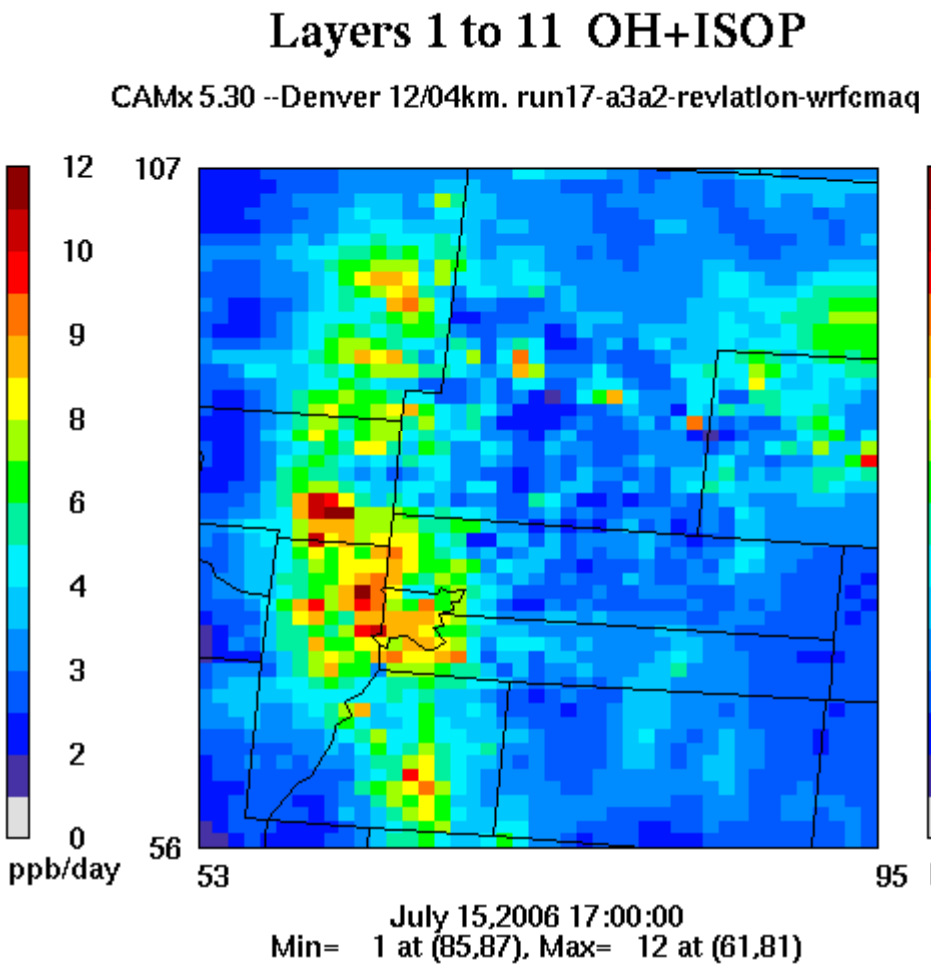
Layer 1 ISOP concentration at 1 PM LDT

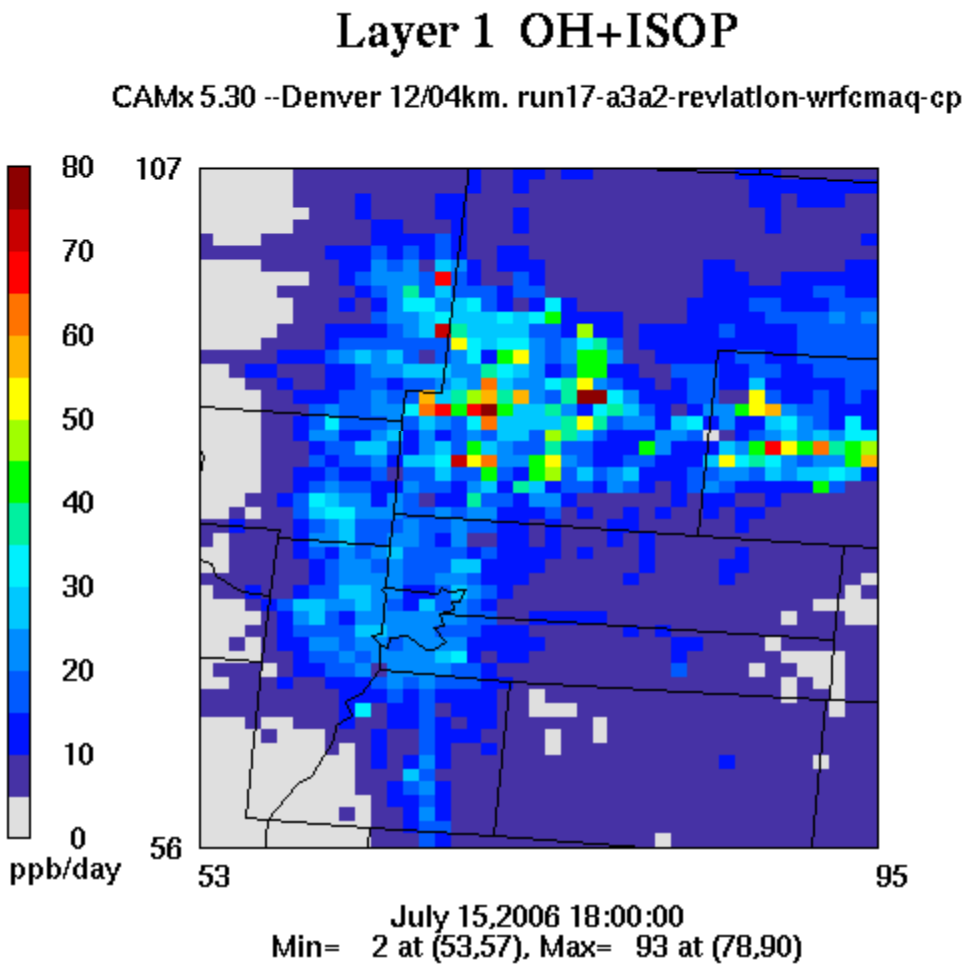


Layer 1 OH+ISOP



When summing over 11 layers, isoprene reacted with OH is largest in the foothills and the Denver area.





Conclusions

- CAMx less reactive than CMAQ in Denver area in initial model runs.
- Ozone Sensitivity to VOC and NOx:
  - Denver and parts of Weld are VOC sensitive
  - Parts of Weld are both VOC and NOx sensitive
  - Ft Collins area is NOx sensitive
- Large contribution from isoprene in Weld county.
- Process Analysis is useful for diagnostic QA and exploration of model results:
  - CPA outputs are most accessible and easiest to visualize.
  - Time intensive.
  - Spatial analysis is complex, but Barron Henderson has developed a python based tool for volume and plume analysis: http://pypa.googlecode.com


Questions?